QUANTITATIVE

CHEMICAL ANALYSIS

TALBOT
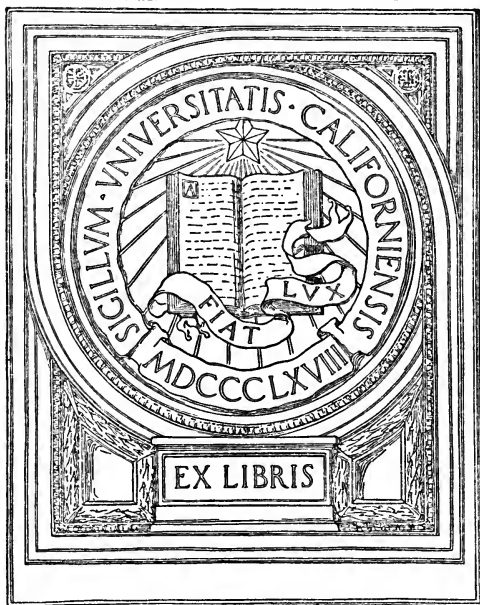
AN INTRODUCTORY COURSE

OF

QUANTITATIVE

CHEMICAL ANALYSIS,

WITH

EXPLANATORY NOTES

AND

STOICHIOMETRICAL PROBLEMS.

BY

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THIRD EDITION.
REVISED AND ENLARGED.

PREFACE.

THIS Introductory Course of Quantitative Analysis has, been prepared to meet the needs of students who are just entering upon the subject, after a course of qualitative analysis. It is primarily intended to enable the student to work successfully and intelligently, without the necessity for a larger measure of personal assistance and supervision than can reasonably be given to each member of a large class. To this end the directions are given in such detail that there is very little opportunity for the student to go astray; but the manual is not, the author believes, on this account less adapted for use with small classes, where the instructor, by greater personal influence, can stimulate independent thought on the part of the pupil.

The method of presentation of the subject is that suggested by Prof. A. A. Noyes' excellent manual of Qualitative Analysis. For each analysis the procedure is given in considerable detail, and this is accompanied by explanatory notes, which are believed to be sufficiently expanded to enable the student to understand fully the underlying reason for each step prescribed. The use of the book should nevertheless be supplemented by classroom instruction, mainly of the character of recitations, and the student should be taught to consult the larger works, such as those of Fresenius, Mohr, and Sutton. The general directions of Part I are intended to emphasize those matters upon which the beginner in quantitative analysis must bestow special care, and to offer some helpful suggestions. The student can hardly be expected to appreciate the force of all the statements contained in these directions, or, indeed, to retain them all in the memory after a single reading, but the instructor, by frequent reference

to special paragraphs as suitable occasion presents itself, can soon render them familiar to the student.

The analyses selected for practice are those comprised in the course of "preliminary quantitative analysis" at the Massachusetts Institute of Technology, and have been chosen, after an experience of some years, as affording the best preparation for more advanced work, and as satisfactory types of gravimetric and volumetric methods. From the latter point of view, they also seem to furnish the best insight into quantitative analysis for those students who can devote but a limited time to the subject, and who may never extend their study beyond the field covered by this manual. The author has had opportunity to test the efficiency of the course for use with such students, and has found the results satisfactory.

In place of the usual custom of selecting simple salts as material for preliminary practice, it has been found advantageous to substitute, in most instances, approximately pure samples of appropriate minerals or industrial products. The difficulties are not greatly enhanced, while the student gains in practical experience.

It has been found expedient with large classes, to allow the whole class to work simultaneously upon the same procedure, for example, that for the determination of chlorine in sodium chloride, since classroom instruction can then be made more effective. Each individual is, however, permitted to work as rapidly as his capacity admits, and to such students as exhibit unusual facility in manipulation, extra analyses are assigned.

The author has been unable to find any work in which such stoichiometrical problems as are constantly met with in the experience of an analyst are dealt with in such detail as to enable the student to fully understand the underlying principles. A chapter has therefore been added in which such problems are presented, and the solutions of certain typical cases are explained. A table of atomic weights and a table of four-place logarithms are appended for convenience.

The analytical procedures, as detailed in this manual, are those dictated by experience in the laboratories of the Institute as giving the best results for purposes of instruction. The author has received many suggestions from standard works, but no attempt has been made to enumerate these in full; nor, on the other hand, is any considerable credit claimed for originality. Criticisms or corrections will be welcomed.

A knowledge of the modern theories of solutions has become so important a possession for even the beginner in quantitative analysis, if he is to view his work from a scientific standpoint, that it has seemed desirable to add a chapter to the present edition, in which these theories are briefly stated. No attempt has been made to treat the subject exhaustively, and the instructor will doubtless find it necessary and desirable to present much in the way of additional detail and illustration. The student should also be urged to think and read for himself.

A few determinations have been added to the list of gravimetric analyses, and the text has been generally revised.

The author wishes to express his appreciation of the kindly reception accorded the earlier editions of this manual, and his obligations to Prof. A. A. Noyes, and to Drs. W. H. Walker and F. J. Moore, Instructors in Analytical Chemistry at the Institute, for helpful suggestions and much kind assistance in its preparation.

<div align="right">Henry P. Talbot.</div>

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PART I.

INTRODUCTION.

A COMPLETE chemical analysis of a body of unknown composition involves the recognition of its component parts by the methods of *qualitative analysis*, and the determination of the proportions in which these components are present by the processes of *quantitative analysis*. The qualitative examination is indispensable if intelligent and proper provisions are to be made for the separation of the various constituents, under such conditions as shall insure accurate, quantitative estimations.

It is assumed that the operations of *qualitative* analysis are familiar to the student, who will find that the reactions made use of in *quantitative* processes are not infrequently those employed for the qualitative detection of the same element; but it should be noted that the conditions must now be regulated with greater care, and in such a manner as to insure the most complete separations possible. For example, in the qualitative detection of sulphates by precipitation as barium sulphate from acid solution, it is not necessary, in most instances, to regard the solubility of the sulphate in hydrochloric acid, while in the quantitative determination of sulphates by this reaction, this solubility becomes an important consideration. The operations of qualitative analysis are, therefore, the more accurate, the nearer they are made to conform to quantitative conditions.

The methods of quantitative analysis are sub-divided, according to their nature, into those of *gravimetric* and *volumetric* analysis. In *gravimetric* processes the constituent to be determined is isolated in the form of some compound possessing a well-established and definite composition, which can be readily and completely separated by filtration, and

weighed either directly, or after ignition. From the weight of this body the amount of the constituent in question is determined.

In *volumetric analysis*, instead of the final weighing of a definite body, a well-defined reaction is caused to take place, wherein the reagent is added in the form of a solution, of which the strength (and hence the value for the reaction in question) is accurately known. The volume of this solution required to complete the reaction then becomes a measure of the substance acted upon. An example will make the distinction clear. The percentage of chlorine in a sample of sodium chloride may be determined by precipitation of the chlorine from a weighed portion as silver chloride, which is separated by filtration, ignited, and weighed (a *gravimetric* process) ; or the sodium chloride may be dissolved in water, and a solution of silver nitrate, containing an accurately known amount of the silver salt in each cubic centimeter, may be cautiously added until precipitation is complete, when the amount of chlorine may be calculated from the number of cubic centimeters of the silver nitrate solution involved in the reaction. This is a *volumetric* process and is equivalent to weighing without the use of a balance.

Volumetric methods are generally more rapid, and frequently capable of greater accuracy, than gravimetric methods.

GENERAL DIRECTIONS FOR QUANTITATIVE WORK.

The following suggestions should be carefully and thoughtfully read ; their adoption will lead to work of a high grade of excellence, while their rejection may often lead to unsatisfactory or careless work.

NEATNESS.

The laboratory desk, and all apparatus, should be scrupulously neat and clean at all times. A sponge should always be ready at hand, and desk and filter-stands should be dry and in good order. Funnels should never be allowed to drip upon the base of the stand. Glassware should always be wiped with a clean, lintless towel just before use.

WASH—BOTTLES.

Wash-bottles, for distilled water, should be made from flasks of about 750 cc. capacity and be provided with gracefully bent tubes, which should not be too long. The jet should be connected with the tube entering the wash-bottle by a short piece of rubber tubing, in such a way as to be flexible, and should deliver a stream about one millimeter in diameter. The neck of the flask may be wound with twine, or covered with wash leather for greater comfort when hot water is used. It is well to provide several small wash-bottles for liquids other than distilled water, which should invariably be clearly labelled.

DESICCATORS.

Desiccators should be filled with fused, anhydrous calcium chloride, over which is placed an iron triangle wound with platinum foil at those points which come into contact with a hot crucible. The cover of the desiccator should be made air-tight by the use of a thin coating of tallow.

Pumice moistened with sulphuric acid may be used in place of the calcium chloride, and is essential in special cases, but for most purposes the calcium chloride, if renewed occasionally and not allowed to cake together, is equally efficient.

Desiccators should never remain uncovered for any length of time. The dehydrating agents rapidly lose their efficiency on exposure to the air.

CRUCIBLES.

Platinum crucibles should be employed for all ignitions and fusions, when possible. All crucibles, whether of platinum or porcelain, must be heated, and cooled in a desiccator before use. This is to insure parallel conditions in separate weighings, which could not be obtained if the crucible were cooled in contact with the air, since a layer of moisture is then condensed on its surface, the amount varying with the humidity of the atmosphere. In the dry air of the desiccator this difficulty is avoided.

Crucibles should be cleaned, heated, and weighed before each analysis.

Platinum crucibles should be frequently scoured, either with sea sand or some preparation of the general character of "sapolio." Constant heating causes a slight crystallization of the surface of the platinum, which, if not removed, penetrates into the crucible. Gentle abrasion of the surface destroys the crystalline structure and prevents further damage. If sea sand is used great care is necessary to keep it from the desk, since beakers are easily scratched by it, and subsequently broken on heating.

Platinum crucibles stained by iron may often be cleaned by the use of potassium acid sulphate, or by heating with ammonium chloride. If the former is used, care should be taken not to heat so strongly as to expel all of the sulphuric acid, since the normal sulphate expands so rapidly on cooling as sometimes to burst the crucible.

Bodies containing metals which might be reduced, with the formation of metallic buttons, must not be treated in platinum crucibles. Fusible alloys of platinum may be formed which ruin the crucible. Compounds of phosphorus or arsenic must not be heated under reducing conditions, since these elements, by contact with the platinum, render it brittle.

Liquids containing free chlorine, aqua regia, or ferric chloride all exert a solvent action upon platinum, the ferric chloride to a lesser degree than the others. Care must be taken to prevent the introduction of platinum into analyses by a disregard of these facts.

Caustic alkalies and peroxides of the alkalies attack platinum freely. Fusions with these fluxes should be made in silver crucibles.

EVAPORATION OF LIQUIDS.

Too great care cannot be taken to prevent loss of solutions during processes of evaporation, either from too violent ebullition, from evaporation to dryness and spattering, or from the evolution of gas during the heating. It may be

stated in general that evaporation upon the steam bath is to be preferred to other methods on account of the impossibility of loss by spattering. If the steam baths are well protected from dust, solutions should be left without covers during evaporation, but solutions which are boiled upon the hot plate, or from which gases are escaping, should invariably be covered. In any case a watch-glass may be supported above the vessel by means of a glass triangle, or other similar device, and the danger of loss of material or contamination by dust be thus avoided.

It is obvious that evaporation is promoted by the use of vessels which admit of the exposure of a broad surface to the air.

Liquids which contain suspended matter (precipitates) should always be cautiously treated, since the presence of the solid matter is frequently the occasion of violent "bumping," with consequent risk to apparatus and analysis.

Liquids should never be transferred from one vessel to another, nor to a filter, without the aid of a stirring rod held firmly against the side or lip of the vessel. When the vessel is provided with a lip it is not usually necessary to use tallow or vaseline to prevent the loss of liquid by running down the side; whenever this seems imminent a *very thin* layer of tallow, applied with the finger to the edge of the vessel, will suffice. The stirring rod, down which the liquid runs, should never be drawn upward in such a way as to allow the solution to collect on the under side of the rim of a beaker.

REAGENTS.

All reagents should be measured, and a record of the amounts used should be made in the notebook.

Whenever it is practicable, the amount of the reagent required should be calculated, and a large excess avoided. Many analyses are spoiled by a neglect of this precaution.

Reagents should be carefully examined for impurities. If these are found, blank analyses must be made, using only the reagents, and the amounts thus found deducted from the weights of contaminated precipitates. Under these cir-

cumstances, the value of the first suggestion in this paragraph is obvious.

The stoppers of reagent bottles should never be laid upon the desk, unless upon a clean watch-glass or paper. The neck and mouth of all such bottles should be kept scrupulously clean, and care taken that no confusion of stoppers occurs.

PRECIPITATION.

From theoretical considerations it appears that no substance is to be regarded as absolutely insoluble in a specific medium, although the solubility of many, which we term insoluble bodies, is less than can be measured by the means at our disposal. Successful precipitation must involve conditions which insure the nearest approximation to insolubility of the precipitated body, and the precipitate must also be in a form favorable for filtration and washing. For crystalline precipitates, the latter condition is fulfilled when the crystals are relatively large. This is often attained by allowing the fine crystals, which first separate, to digest in contact with the hot liquid from which they have fallen. During this digestion the smaller crystals, which are very slightly more soluble than the larger ones, redissolve, and the solution, which is supersaturated as regards the larger crystals, allows the latter to separate. This transfer is further promoted by the influence of surface tension, which tends to reduce the surface of the solid, *i. e.,* to increase the size of the individual crystals.

Certain amorphous bodies, such as ferric hydroxide, aluminum hydroxide, and silicic acid may pass into a colloidal state, in which they form semi-solutions. This may happen if an attempt is made to precipitate them from solutions which are free from other salts. These rarely occur in analysis, but during the washing of these precipitates such semi-solutions may sometimes be formed, unless some salt is added to the wash water. In cases where the addition of a salt to the wash water is impracticable, the precipitate should be digested for some time on the steam bath with the original solution, a procedure which lessens its tendency to pass into the colloidal state.

In all precipitations the reagent should be added slowly, with constant stirring, and should be hot when circumstances permit. The slow addition is less likely to occasion contamination of the precipitate by the inclosure of other substances which may be in the solution, or of the reagent itself.

For the complete removal of precipitates from containing vessels, it is often necessary to rub the sides of these vessels to loosen the adhering particles. This can best be done by slipping over the end of a stirring rod a piece of soft rubber tubing, which has been well washed to remove loose fragments, or by using a piece of sheet rubber, which may be folded over the rod and cemented together by moistening the surfaces with benzene. The sides of the beaker can then be rubbed with the covered rod.

All stirring rods should have the ends rounded in the flame to avoid scratching the beakers.

FILTRATION, AND THE TESTING OF FILTRATES AND WASHINGS.

Distilled water should be employed in all quantitative work, and filtration should be made only through "washed filters," *i. e.*, those which have been treated with hydrochloric and hydrofluoric acids, and which, on incineration, leave a small and definitely known weight of ash. Such filters are readily obtainable in the market.

Funnels should be selected which have an angle as near 60° as possible, and with a narrow stem about six inches in length. The filter should be accurately folded to fit the funnel, and placed so that the top of the filter is about one-fourth inch below the top of the funnel. Under no circumstances should the filter ever extend above the edge of the funnel, as it is then utterly impossible to effect complete washing.

To test the efficiency of the filter, fill it with distilled water; this water should soon fill the neck completely, forming a continuous column of liquid which, by its hydrostatic pressure, produces a gentle suction, materially promoting the rapidity of filtration. Unless the filter allows

a free passage of water under these conditions, its use is likely to prove a source of annoyance.

The use of a vacuum pump to promote filtration is rarely altogether advantageous in quantitative analysis, if paper filters are employed. The tendency of precipitates to pass through the pores of the filter is increased, and this source of danger more than compensates for the possible gain in time. Exception may be made in the case of such precipitates as the hydroxides of chromium, aluminum, or iron, and of silicic acid, but whenever suction is applied, the point of the paper filter must be supported by a perforated platinum cone or a small "hardened filter" of parchment. The rate of filtration is often greater when an asbestos felt (Gooch filter) is used (see page 27 for a description), and the possibility of a substitution of this for the paper filter should always be considered.

When the filtrate is received in a beaker, the stem of the funnel should touch the side of the receiving vessel to avoid loss by spattering. Neglect of this precaution is a frequent source of error.

The vessels which contain the initial filtrate should *always* be replaced by clean ones, properly labelled, before the washing of a precipitate begins. In many instances a finely divided precipitate, which shows no tendency to pass through the filter at first, while the solution is relatively dense, appears at once in the washings. Under such conditions the advantages accruing from the removal of the first filtrate are obvious, both as regards the diminished volume requiring refiltration, and also the lesser amount of washing subsequently required.

Much time may often be saved by washing precipitates by decantation, *i. e.*, by pouring over them, while still in the original vessel, considerable volumes of wash-water and allowing them to settle. The supernatant, clear wash-water is then decanted through the filter, so far as is practicable without disturbing the precipitate, and a new portion of wash-water is added. This procedure can be employed to special advantage with gelatinous precipitates, which fill up the pores of the filter paper. As the medium from which

the precipitate is to settle becomes less dense, it subsides less readily, and it becomes necessary to transfer it to the filter and complete the washing there.

A precipitate should never fill the filter completely, and the wash-water should be applied at the top of the filter, above the precipitate. It may be shown mathematically that the washing is most rapidly accomplished by filling the filter well to the top with wash-water each time, and allowing it to drain completely after each addition, but that when a precipitate is to be washed with the least possible volume of liquid the latter should be applied in repeated small quantities. For a discussion of this matter and the phenomena of adsorption, the student is referred to *Ostwald's Foundations of Analytical Chemistry*, page 15, *et seq.*

Gelatinous precipitates should not be allowed to dry before complete removal of foreign matter is effected. They are likely to shrink and crack, and subsequent additions of wash-water pass through these channels only.

Solutions should be filtered while hot, as far as possible, since the motion of the liquid through the pores of a filter is retarded by internal friction, and this, for water at 100° C., is less than one sixth of the resistance at 0° C.

All filtrates and wash-waters *without exception* should be properly tested. In testing the latter an amount not less than 3 cc. should be taken for the *final* test.

It is impossible to trust to one's judgment with regard to the washing of precipitates ; the washings from *each precipitate* of a series simultaneously treated must be tested, since the rate of washing will often differ materially under apparently similar conditions. *No exception can ever be made to this rule.*

The habit of placing a clean filter paper under the receiving beaker during filtration, is one to be commended. On this paper a record of the number of washings can very well be made as the portions of wash-water are added.

IGNITION OF PRECIPITATES.

The larger number of precipitates may, if proper precautions are taken, be ignited without previous drying. If, how-

ever, such precipitates can be dried without loss of time to the analyst (as, for example, over night), it is well to submit them to this process. It should, nevertheless, be remembered that a partially dried precipitate requires as much, or more care during ignition than a thoroughly moist one.

The precipitate, with the filter folded over it, should be placed well at the base of the crucible, which should then be placed so far above the flame of the lamp that no violent escape of steam is possible. When the filter and contents have dried, the crucible should be placed on its side without the cover, and the heat should be gently increased until the filter chars, but should *never* be increased beyond this point until all volatile matter from the dry distillation of the filter paper has been expelled without taking fire. Much annoyance will be avoided by observing this point.

During this preliminary heating the flame should be placed near the mouth of the crucible, but in all subsequent heating the flame of the lamp should be well at the base of the crucible, as it is inclined upon its side, to allow a ready access of oxygen and to avoid the entrance of unburned (reducing) gases. When the filter has charred, the heat should be raised to redness until ignition is complete. The heating of precipitates over the blast lamp is to be avoided unless specially directed.

The limited number of instances in which the precipitate must be separated from the filter preliminary to ignition will be treated of as they occur.

USE AND CARE OF BALANCES.

The analytical balance is a delicate instrument, which will perform excellent service under careful treatment, but such treatment is an essential condition if its accuracy is to be depended upon. The following rules may be regarded as embodying the important points involved in the use of a balance, but no rules can do away with the necessity for a sense of personal responsibility on the part of each student, since by carelessness he can render inaccurate not only his own analyses, but those of other students using the balance :

1. The balance pans should be brushed off and the adjustment of the balance tested before use, particularly where several persons use the same instrument.

To determine whether or not the balance is in adjustment, note (1) whether it is level; (2) whether the pointer rests at zero when the beam is lifted from its knife-edges, and also when lowered so that the pan arrests touch the scale pans; (3) that the mechanism for raising and lowering the beams works smoothly; (4) that the pan arrests touch the pans when the beam is lowered; and (5) that the needle swings equal distances on either side of the zero-point when set in motion without any load on the pans. If the latter condition is not absolutely fulfilled, the balance should be adjusted, unless the variation is not more than one division on the scale; it is often better to make a proper allowance for this zero error rather than to disturb the balance by an attempt at correction.

Unless a student thoroughly understands the construction of a balance he should never attempt to make adjustments, but should apply to the instructor in charge. For a discussion of the construction and essential characteristics of a balance the student is referred to *Fresenius' Quantitative Analysis*.

2. The beam should never be set in motion by lowering it forcibly upon the knife-edges, nor by touching the pans, but rather by means of the rider (unless the balance be provided with some of the newer devices for the purpose), and the swing should be arrested only when the needle passes the zero on the scale, otherwise the knife-edges become dull. For the same reason the beam should never be left upon its knife-edges, nor should weights be removed from, or placed on the pans without supporting the beam, except in the case of the small fractional weights.

3. In testing the weight of a body, the weights should be applied in the order in which they occur in the weight-box (not at haphazard), and the weight should be recorded first by noting the weights missing from the weight-box, and that record subsequently checked as these weights are

taken from the pan. This practice will often avoid or detect errors.

4. The balance-case should always be closed during the final weighing, when the rider is used, to protect the pans from the influence of air currents.

Before the final determination of an exact weight the beam should always be lifted from the knife-edges and again lowered into place, as it frequently happens that the scale pans are twisted by the impact of the weights, the beam being virtually lengthened or shortened. Lifting the beam restores the proper alignment.

After the weighing is finished, the weights should always be replaced in their proper places in the weight-box and the rider taken from the beam.

5. No chemical substance should ever be placed directly upon the balance-pan. Every substance or vessel weighed should be *dry* and *cold*. A warm object occasions the formation of air currents, which vitiate the accuracy of the weight.

6. Above all, if any damage be done to a balance, if any substance be spilled upon the pans, or if the mechanism appear to be deranged, the matter should receive immediate attention, and should be reported at once to the instructor in charge. In the majority of instances serious damage can be averted by prompt action, when delay might ruin the balance.

NOTEBOOKS.

Notebooks should contain, beside the record of observations, descriptive notes. All records of weights should be placed upon the right-hand page, while that on the left is reserved for the notes, calculations of factors, or the amount of reagents required.

The neat and systematic arrangement of the records of analyses is of the first importance, and is an evidence of careful work and an excellent credential. Of two notebooks in which the results may be, in fact, of equal value as legal

evidence, that one which is neatly arranged will carry with it greater weight.

All records should be dated, and all observations should be recorded at once in the notebook. The making of records upon loose paper is a practice to be deprecated, as is also that of copying original entries into a second notebook. The student should accustom himself to orderly entries at the time of observation.

The descriptive notes should mention any special difficulties encountered in the analyses and the remedies applied, and also incidents in the course of the analysis, if any, which may possibly influence the results injuriously. All analyses should be made in duplicate, and in general a close agreement in results should be expected. It should, however, be remembered that a close concordance of results in "check analyses" is not conclusive evidence of the accuracy of those results, although the probability that such is the case is, of course, considerably enhanced. The satisfaction in obtaining "check results" in such analyses must never be allowed to interfere with the critical examination of the procedure employed, nor must they ever be regarded as in any measure a substitute for absolute truth and accuracy.

ECONOMY OF TIME.

An economical use of laboratory hours is best secured by acquiring a thorough knowledge of the character of the work to be done before undertaking it, and then by so arranging the work that no time shall be wasted during the evaporation of liquids and like time-consuming operations. To this end the student should read thoughtfully not only the procedure, but the explanatory notes as well, before any step is taken in the analysis.

Several analyses should be in progress at once and confusion carefully guarded against by a free use of labels.

In general, economy of time results from the filtration of several solutions at once, since the washing of five or more precipitates may frequently be accomplished in the time requisite for any one, if taken alone.

ACCURACY AND INTEGRITY DEMANDED.

The fundamental conception of quantitative analysis implies a necessity for all possible care in guarding against loss of material, or the introduction of foreign matter. All filters and solutions should be covered to protect them from dust, just as far as is practicable, and every particle of solution or precipitate must be regarded as invaluable for the success of the analysis.

In this connection it must also be emphasized that only the operator himself can know the whole history of an analysis, and only he can know whether his work is worthy of full confidence. No work should be continued for a moment after such confidence is lost, but should be resolutely discarded as soon as a cause for distrust is fully established. The student should determine to put forth his best efforts in *each* analysis ; it is well not to be too ready to condone failures and to " begin again," as much time is lost in these fruitless attempts. *Nothing less than absolute integrity is or can be demanded of a quantitative analyst, and any disregard of this principle, however slight, is as fatal to success as lack of chemical knowledge or inaptitude at manipulation can possibly be.*

PART II.

GRAVIMETRIC ANALYSIS.

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE.

PREPARATION.

THE preparation of chemically pure sodium chloride from the commercial article may be effected as follows :

Procedure. — Weigh out, upon rough balances, about 50 grams of a sample of "table salt," cover this with 120 cc. of distilled water, stir until the water is saturated, and filter. To the filtrate add concentrated hydrochloric acid (sp. gr. 1.20) until the chloride begins to separate, then pass into the solution gaseous hydrochloric acid. This acid should be generated in a flask, from rock salt and commercial sulphuric acid. The gas should be washed by passing it through concentrated, aqueous hydrochloric acid, and the delivery-tube should terminate in a 2-inch funnel, placed mouth downward, to prevent the clogging of the delivery-tube by the separated salt. When the separation of the salt has apparently ceased, remove it by filtration upon a paper disc placed upon a perforated porcelain plate (a Witt filter), and drain by suction. Wash the chloride with 25 cc. of hydrochloric acid (sp. gr. 1.12) in successive small portions, allowing the precipitate to drain completely after each addition. Wash finally with a small quantity (5 cc.) of water, and test this wash-water for sulphates. If sulphates are found, the washing with hydrochloric acid must be continued. When freed from sulphates, transfer the precipitate to a porcelain or platinum dish, or crucible, and heat until decrepitation ceases. The chloride should then be allowed

to cool in a desiccator, and be placed in a weighing-tube (like a small test-tube), which should be kept tightly stoppered.

Notes. — 1. The commercial grades of table salt contain, beside sodium chloride, chlorides or sulphates of magnesium, calcium, or potassium, the two first-named causing the salt to absorb moisture. When hydrochloric acid is added to a saturated solution of the salt, sodium chloride is thrown down, leaving the impurities in solution. The principle underlying this separation may be briefly stated by saying that the solution is saturated with respect to chlorine radicals (chlorine ions, more properly), and when more of these chlorine ions are added, in the form of the readily soluble hydrochloric acid, some of those in combination with sodium are forced out of solution in the form of the relatively insoluble sodium chloride.

2. The precipitation of the sodium chloride might be effected more quickly by the addition of liberal quantities of concentrated aqueous hydrochloric acid, but its purity is less certain under those conditions. The slow separation, caused by the absorption of the gas, is more favorable to the isolation of a pure product, and the process is also somewhat more economical.

3. Since the sodium chloride is not insoluble in either the acid or the water used for washing, it is essential that these should be used in as small quantities as is practicable. Note the statement on page 15 concerning the most efficient method of washing a precipitate with a limited quantity of liquid.

4. The heating of the chloride is essential to expel any excess of hydrochloric acid held by the salt, and to remove moisture inclosed between crystal surfaces. The escape of this moisture is the cause of decrepitation. Even the pure salt is slightly hygroscopic ; hence the necessity for cooling in the dry air of the desiccator and for preservation in stoppered tubes.

ANALYSIS.

The sodium chloride, prepared as above, is ready for analysis, and if the preparation has been carefully made, the percentage of chlorine found on analysis should agree closely with that calculated from the symbol.

Procedure. (*a*) Carefully clean the weighing-tube containing the sodium chloride, handling it as little as possible with the moist fingers, and weigh it accurately to 0.0001 gram, recording the weight at once in the notebook. Hold the tube over the top of a No. 3 lipped beaker, and cautiously remove the stopper, noting carefully that no particles fall from it, or from the tube, elsewhere than into the beaker. Pour out a small portion of the chloride, replace the stopper, and de termine by approximate weighing how much has been removed. Continue this procedure until 0.25–0.30 gram has been taken from the tube, then weigh accurately and record the weight beneath the first in the notebook. The difference of the two weights represents the weight of the chloride taken for analysis. Again weigh a second portion of 0.25–0.30 gram into a second beaker of the same size as the first. The beakers should be plainly marked to correspond with the entries in the notebook. Dissolve each portion of the chloride in 150 cc. of distilled water, and add about ten drops of nitric acid (sp. gr. 1.20). Calculate the volume of a silver nitrate solution required to effect complete precipitation in each case, and add slowly about 5 cc. in excess of that amount, with constant stirring. Heat the solutions cautiously to boiling, stirring occasionally, and continue the heating and stirring until the precipitates settle promptly, leaving a nearly clear supernatant liquid. This heating should not take place in direct sunlight. The beaker should be covered with a watch-glass, and both boiling and stirring so regulated as to preclude any possibility of loss of material. Add to the clear liquid one or two drops of silver nitrate solution, to make sure that an excess of the reagent is present. Prepare two washed filters (9 cm. in diameter), bearing in mind the precautions mentioned on pages 13 and 14, and pass the liquid through the filter, leaving the chloride in the beaker as far as possible. Wash the precipitates two or three times with hot water, by decantation, transfer them to the filter by means of a stream from the wash-bottle, with the aid of a feather or a rubber tip on a stirring rod, if need be. Finally remove the main filtrate, replace by a clean beaker,

and wash the filters and precipitates until 3 cc. of the washings show no cloudiness with a *drop* of hydrochloric acid. The funnels should then be covered with a filter paper which has been previously moistened and stretched over the sides of the funnel, to which it will adhere on drying. It should be properly labelled with the student's name and desk number, and then placed in a drying closet, at a temperature of about 100–110° C., until completely dry. Put the filtrate containing the silver nitrate aside in a suitable receptacle for "silver residues," from which the silver can be recovered.

The perfectly dry filter is then opened over a circular piece of clean, smooth, glazed paper about six inches in diameter, placed upon a larger piece about twelve inches in diameter. The precipitate is removed from the filter as completely as possible, by rubbing the sides gently together, or by scraping them cautiously with a feather, which has been cut close to the quill and is slightly stiff. In either case, care must be taken not to rub off any considerable quantity of the paper, nor to lose silver chloride in the form of dust. Cover the precipitate on the glazed paper with a watch-glass, to prevent loss of fine particles and to protect it from dust. Fold the filter paper carefully, as it was when it came from the funnel, roll it into a small cone, and wind loosely around *the top* a piece of small platinum wire. Hold the filter by the wire over the proper porcelain crucible, ignite it, and allow the ash to fall into the crucible. Place the crucible upon a clean clay triangle, on its side, and ignite, with the flame well at its base until all the carbon of the filter has been consumed. Allow the crucible to cool, add two drops of nitric acid and one drop of hydrochloric acid, and heat *very cautiously*, to avoid spattering, until the acids have been expelled; then transfer the main portion of the precipitate from the glazed paper to the cooled crucible, placing the latter, for the purpose, on the larger piece of glazed paper and brushing the precipitate from the smaller piece into it, sweeping up all particles belonging to the determination.

Moisten the precipitate with two drops of nitric acid and

one drop of hydrochloric acid, and again heat with great caution until the acids are expelled and the precipitate is white, after which the temperature is *gradually* raised until the silver chloride begins to fuse. The crucible is then cooled in a desiccator and weighed, after which the heating (without the addition of acids) is repeated, and it is again weighed. This must be continued until the weight is constant within 0.0003 gram in two consecutive weighings. Deduct the weight of the crucible, and calculate the weight of chlorine in the silver chloride, and subsequently the percentage in the sample of sodium chloride taken for analysis. Consult Part V, page 132.

Notes.— 1. The nitric acid is added before precipitation to lessen the tendency of the silver chloride to carry down with it other substances which may be present in the solution. A large excess of the acid would exert a slight solvent action upon the chloride.

2. The solution should not be boiled after the addition of the nitric acid, before the presence of an excess of silver nitrate is assured, since a slight interaction between the nitric acid and the sodium chloride is possible, by which a loss of chlorine, either as such or as hydrochloric acid, might ensue. The presence of an excess of the precipitant can usually be recognized at the time of its addition, by the increased readiness with which the precipitate clots together and settles.

3. The precipitate should not be exposed to strong sunlight, since by its action a reduction of the silver chloride is effected, accompanied by a loss of chlorine. The superficial alteration which the chloride undergoes in diffused daylight is not fatal to the accuracy of the determination, since the slight loss of chlorine may be counteracted by the treatment of the precipitate with nitrohydrochloric acid, as noted below.

4. The precipitate must be washed with hot water until it is absolutely free from silver and sodium nitrates. It may be assumed that the sodium is also completely removed when the wash-water shows no evidence of silver. It must be borne in mind that silver chloride is somewhat soluble in hydrochloric acid, and only a single drop should be added. The

washing should be continued until no cloudiness whatever can be detected in 3 cc. of the washings. ,

5. The separation of the silver chloride from the filter is essential, since the burning carbon of the paper would reduce a considerable quantity of the precipitate to metallic silver, and its complete reconversion to the chloride within the crucible, by means of acids, would be accompanied by some uncertainty. The small amount of precipitate which adheres to the filter is partially reduced to metallic silver during the ignition, but this small quantity can be dissolved in the nitric acid which is added, and completely reconverted to chloride by the hydrochloric acid. The subsequent addition of these two acids to the main portion of the precipitate restores the chlorine to the chloride reduced by the sunlight.

The platinum wire is wrapped around the top of the filter during its incineration, to avoid contact with any reduced silver which might come from the reduction of the precipitate. If the wire was placed nearer the apex, such contact could hardly be avoided.

6. Silver chloride should not be heated to complete fusion, since a slight loss by volatilization is possible at higher temperatures. The temperature of fusion is not always sufficient to destroy filter shreds; hence these should not be allowed to contaminate the precipitate.

7. The ignited precipitate of silver chloride should be placed in the jar for "silver residues." The crucible may be cleaned by placing in it some granulated zinc and dilute sulphuric acid. The chloride is soon loosened, and may be detached.

8. Silver chloride is practically insoluble in water and dilute nitric acid, slightly soluble in strong nitric acid, and appreciably so in strong hydrochloric acid. It is also slightly soluble in hot concentrated solutions of silver nitrate. The chloride is readily soluble in aqueous ammonia and in solutions of potassium cyanide and sodium thiosulphate.

9. Stoppers in weighing-tubes are likely to change in weight from the varying amounts of moisture absorbed from the atmosphere. It is, therefore, necessary to confirm the recorded weight of a tube which has been unused for some time, before weighing out a new portion of substance from it.

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE, WITH
THE USE OF A GOOCH FILTER.

A commercial sample of table salt may advantageously be
substituted for the pure sodium chloride, if the latter has
already been examined. The table salt should be heated
until decrepitation ceases, and cooled in a desiccator.

Procedure. — (*b*) Weigh out two portions of the sub-
stance, each weighing about 0.25 gram, and precipitate
the silver chloride as described in procedure (*a*). Mean-
while prepare a Gooch filter as follows : Select a small
glass funnel, 1 to 1¼ inches in diameter, and stretch over
its mouth a piece of rubber-band tubing ("bill-tie tubing")
about 1 inch wide and 1½ inches long. This should be
drawn down on the sides of the funnel until it holds firmly,
leaving an opening at the center of the mouth of the funnel,
into which a perforated porcelain crucible (Gooch crucible)
is fitted. The rubber should be drawn up around the sides
of the crucible until it is air-tight. Fit the glass funnel
into the stopper of a filter bottle, and connect it with the
vacuum pump. Suspend some finely divided asbestos, which
has been washed with acid, in 20 to 30 cc. of water ; allow
this to settle, pour off the very fine particles, and then
pour the rest cautiously into the crucible until an even felt
of asbestos, not over $\frac{1}{32}$ inch in thickness, is formed. A
gentle suction must be applied while preparing this felt.
Wash the felt thoroughly with distilled water until all
fine or loose particles are removed, then place the cruci-
ble in a small beaker, and place both in a drying closet at
130° C. for 30 to 40 minutes. Cool the crucible in a des-
iccator, and weigh. Heat again for 20 to 30 minutes, cool,
and again weigh, repeating this until the weight is constant
within 0.0003 gram. The filter is then ready for use.

Replace the crucible in the funnel, and apply a gentle
suction, *after which*, pour in the solution to be filtered, with-
out disturbing the asbestos felt. When pouring liquid into
a Gooch filter, hold the stirring rod well down in the cru-

cible, so that the liquid does not fall with any force upon the asbestos.

Transfer the whole of the precipitate to the filter, and wash thoroughly with hot water until free from soluble silver salts, then dry, at 130° C., to a constant weight. The percentage of chlorine may be calculated from the weight of silver chloride.

Notes. — 1. The asbestos should be of the finest quality and capable of division into minute fibrous particles. A coarse felt is not satisfactory.

The use of the Gooch filter commends itself strongly when a considerable number of halogen determinations are to be made, since successive portions of the silver halides may be filtered on the same filter, without the removal of the preceding portions, until the crucible is about two thirds filled. The use of a perforated disc of porcelain or platinum, which may be placed upon the top of the asbestos felt, serves to protect it in some measure, but it is obvious that care should be taken to avoid loosening the felt at the edges as the liquid is poured upon it. If the felt is properly prepared, filtration and washing are rapidly accomplished on this filter, and this factor, combined with possibility of collecting several precipitates on the same filter, are strong arguments in favor of its use with any but gelatinous precipitates. If perforated platinum crucibles are employed, which can be fitted into a platinum cap after removal from the funnel, the precipitates can be ignited over the flame of a lamp as in an ordinary platinum crucible. The asbestos is apt to curl away from the edges during such heating, and if the same filter be used for a second time, great care is required to prevent loss of asbestos.

2. A funnel tube, made from stout glass tubing about $1\frac{1}{4}$ inch inside diameter and 3 inches long, to which is attached a tube of suitable size and length to pass through a rubber stopper, may be substituted for the glass funnel above prescribed. It is then only necessary to cover the upper edges of this tube with rubber. The crucible may be pressed into it, and makes air tight connections.

DETERMINATION OF IRON AND OF SULPHUR IN FERROUS AMMONIUM SULPHATE.

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O.$
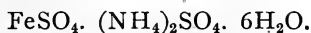
DETERMINATION OF IRON.

Procedure. — Select a quantity of perfectly clear crystals of the salt sufficient to fill a weighing tube. · Weigh out, into two No. 4 lipped beakers, two portions of about 1 gram each, and dissolve these in 50 cc. of water, to which 1 cc. of hydrochloric acid (sp. gr. 1.12) has been added. Heat the solution to boiling, and while at the boiling point add nitric acid (sp. gr. 1.42), *drop by drop* (noting the volume used), until the brown coloration, which appears after the addition of a part of the nitric acid, gives place to a yellow or red. Avoid a large excess of nitric acid, but be sure that the action is complete. Pour this solution cautiously into about 200 cc. of water, containing a slight excess of ammonia. Calculate for this purpose the amount of aqueous ammonia required to neutralize the acids added, and also to precipitate the iron as ferric. hydroxide from the weight of the ferrous ammonium sulphate taken for analysis. The volume thus calculated will be a slight excess over that actually required, since a part of the acids are consumed in the oxidation process, or are volatilized. Heat the solution to boiling, and allow the precipitated ferric hydroxide to settle. Decant the clear liquid through a washed filter (9 cm.), keeping as much of the precipitate in the beaker as possible. Wash once by decantation with 100 cc. of hot water, and then transfer the bulk of the precipitate to the filter. Dissolve the iron from the filter with hot hydrochloric acid, and collect the solution in the beaker in which precipitation took place. Add 3 cc. of nitric acid (sp. gr. 1.42), boil for a few moments, and again pour into an excess of ammonia. Wash the precipitate twice by decantation, and finally throw it on the filter, and wash continuously with hot water until 3 cc. of the washings show no evidences of the presence of chlorides when tested with silver nitrate, acidified with nitric

acid.—The filtrate and washings are combined with those
from the first precipitation.

The moist precipitate is placed in a platinum crucible
which has been previously heated, cooled in a desiccator,
and weighed. It is then treated according to the directions
for "Ignition of Precipitates," page 16. When the volatile
matter of the filter has been expelled, raise the temperature
to the full heat of the burner for fifteen minutes, and finally
heat over the blast lamp, with the crucible covered, for three
minutes. Cool and weigh. Repeat the strong heating
until the weight is constant within 0.0003 gram. Exercise
great care when heating over the blast lamp that a small
flame is used, and that this is directed against the bottom
of the crucible in such a way as to preclude the entrance
of unburned or reducing gases into it, by reflection from
the edges of the cover. From the weight of ferric oxide
(Fe_2O_3) calculate the weight of iron (Fe) and the percent-
age of the latter in the sample.

Notes. — 1. If a selection of *pure* material for analysis is
to be made, those crystals which are cloudy are to be avoided,
on account of loss of water of crystallization ; and also those
which are red, indicating the presence of ferric iron. If, on
the other hand, the value of an *average sample* of the material
is desired, it is preferable to grind the whole together, mix
thoroughly, and take from the mixture a sample for analysis.

2. The hydrochloric acid is added to prevent the precipi-
tation of basic ferric salts during solution, as a result of a par-
tial oxidation of the iron in the absence of free acid. The
nitric acid oxidizes the ferrous iron, after attaining a mod-
erate strength, with the formation of an intermediate nitroso-
compound similar in character to that formed in the "ring-
test" for nitrates. The nitric oxide is driven out by heat,
and the solution then shows by its color the presence of ferric
chloride. A drop of the oxidized solution may be tested on a
watch-glass with potassium ferricyanide, to insure the absence
of ferrous salts. This oxidation of the iron is necessary, since
ferrous salts are not completely precipitated by ammonia.

3. The ferric hydroxide tends to carry down some sul-
phuric acid in the form of basic ferric sulphate. This ten-

dency is lessened if the solution of the iron is added to an excess of ammonia, since under these conditions immediate and complete precipitation of the hydroxide ensues ; whereas, by the gradual neutralization with ammonia, the opportunity for the local formation of a neutral solution within the liquid, and consequent deposition of a basic sulphate, is favored. Even with this precaution the entire absence of sulphates from the first iron precipitate is not assured. It is, therefore, redissolved and again thrown down by ammonia. The organic matter of the filter paper may occasion a partial reduction of the iron during solution, with consequent possibility of incomplete precipitation with ammonia. The nitric acid is added to reoxidize this iron.

4. By the ignition of ferric oxide with ammonium chloride, volatile ferric chloride is formed, with consequent loss of iron. The precipitate must, therefore, be completely washed. The washings are acidified with nitric acid, before testing with silver nitrate, to destroy the ammonia, which is a solvent of silver chloride.

The use of suction to promote filtration and washing is permissible, though not prescribed. The precipitate should not be allowed to dry during the washing, for reasons stated on page 15.

5. To avoid errors arising from the solvent action of ammoniacal liquids upon glass, the iron precipitate should be filtered without unnecessary delay.

6. The directions for the ignition of precipitates must be closely followed. A ready access of atmospheric oxygen is of special importance, to insure the reoxidation to ferric oxide of any iron which may be reduced to magnetic oxide during the combustion of the filter. The final heating over the blast lamp is essential for the complete expulsion of the last traces of water from the hydroxide.

7. Ignited ferric oxide is somewhat hygroscopic, on which account the weighings must be promptly completed after removal from the desiccator. In all weighings after the first, it is well to place the weights upon the balance pan before removing the crucible from the desiccator. It is then only necessary to move the rider to obtain the weight.

8. Ferric hydroxide is practically insoluble in ammoniacal liquids, in the presence of ammonium salts, but the corre-

sponding hydroxides of aluminum and chromium are partially redissolved by an excess of ammonia. Chromium hydroxide is much the most soluble of the three. In other respects the gravimetric determination of these two metals is comparable with that of iron.

For a further statement of the properties of these bodies the student is referred to *Fresenius' Quantitative Analysis*, under "Forms."

DETERMINATION OF SULPHUR.

Procedure. — Add to the combined filtrates from the ferric hydroxide, hydrochloric acid in moderate excess, and evaporate to dryness on the water bath. Add 10 cc. of hydrochloric acid (sp. gr. 1.12) to the residue, and again evaporate to dryness on the bath. Dissolve the residue in water, filter if not clear, transfer to a No. 5 lipped beaker, dilute to about 400 cc., and cautiously add hydrochloric acid until the solution shows a distinctly acid reaction. Heat the solution to boiling, and add *very slowly*, and with constant stirring, 20 cc. in excess of the calculated amount of hot barium chloride solution (which should contain about 20 grams $BaCl_2$, $2H_2O$ per liter). Continue the boiling for about two minutes, allow the precipitate to settle, and decant the liquid at the end of a half hour. Replace the beaker containing the original filtrate by a clean beaker, wash the precipitated sulphate by decantation with hot water, and subsequently upon the filter, until it is freed from chlorides. The filter is then transferred to a platinum crucible and ignited, as described on page 16, until the weight is constant.

To test the purity of the precipitates, mix each, in the crucible, with five to six times its weight of sodium carbonate. This can best be done by placing the crucible on a piece of glazed paper and stirring the mixture with a clean, dry stirring rod, which may finally be wiped off with a small fragment of filter paper, the latter being placed in the crucible. Cover the crucible and heat over a Bunsen or Tirrill burner until a quiet liquid fusion ensues. As the fused mass cools, insert in it a piece of platinum wire, coiled so that it will hold securely in the solidified mass. When solidification is

complete, replace the lamp under the crucible and heat only long enough to cause the outside of the mass to fuse. Now allow the crucible to cool completely, when the mass may frequently be at once drawn out of the crucible by the wire. If it still adheres, a cubic centimeter or so of water may be placed in the cold crucible and cautiously brought to boiling, when the cake will become loosened, and may be removed on the wire and suspended in about 250 cc. of distilled water to dissolve.

Extract the residue of barium carbonate thoroughly with water, taking care to clean the crucible completely. Filter off the carbonate, and wash it with hot water, testing the washings for sulphate, and preserving any precipitates which appear in these tests. Acidify the filtrate with hydrochloric acid until just acid, bring to boiling, and add hot barium chloride solution slowly, as before. Add also any tests from the washings in which precipitates have appeared. Filter, wash, ignite, and weigh. Compare the results with those first obtained, and calculate the weight of sulphur in the barium sulphate, and from that the percentage in the ferrous ammonium sulphate.

Notes. — 1. Barium sulphate, in a larger measure than most substances, tends to carry down other bodies which are present in the solution from which it separates, even when these other bodies are relatively soluble. This is notably true in the case of nitrates and chlorates of the alkalies, and of iron, and, since in this analysis ammonium nitrate has resulted from the neutralization of the excess of nitric acid added to oxidize the iron, it is essential that this should be destroyed by repeated evaporation with a relatively large quantity of hydrochloric acid. During evaporation a mutual decomposition of the two acids takes place, and the nitric acid is finally decomposed and expelled by the excess of hydrochloric acid.

2. The precipitation of the sulphur as barium sulphate might take place in the presence of the iron, but under these conditions the likelihood of contamination of the sulphate by iron would be considerable, and a purification of the precipitate would be unavoidable. On the other hand, ferric chlo-

ride exerts a slight solvent action upon the barium sulphate. For these reasons it is preferable to precipitate the iron before proceeding to the determination of the sulphur.

3. Barium sulphate is slightly soluble in hydrochloric acid, even dilute; hence only the smallest excess should be added over the amount required to acidify the solution. Recent investigations show that the presence of an excess of the barium chloride lessens the solubility of the sulphate in the acid. An addition of 20 cc. of solution in excess is, therefore, prescribed, but, for the reasons stated in Note 1, this excess of chloride should not be too large, and for the same reasons the reagent should be added very slowly, and with constant stirring. It has been shown that the rapid addition leads to a slight co-precipitation of the chloride, which cannot be washed out of the sulphate.

4. The precipitation of the barium sulphate is probably complete at the end of a half-hour, and the solution may safely be filtered at the expiration of that time, if it is desired to hasten the analysis.

As noted on page 12, many precipitates of the general character of this sulphate tend to grow more coarsely granular if digested for some time with the liquid from which they have separated. It is, therefore, well to allow the precipitate to stand in a warm place for several hours before filtration, whenever practicable, to promote ease of filtration. The filtrate and washings should, however, always be carefully examined for minute quantities of the sulphate which may pass through the pores of the filter. This is best accomplished by imparting to the liquid a gentle rotary motion, when the sulphate, if present, will collect in the center of the beaker. All filtrates in this, and other determinations, must be tested for complete precipitation, by adding to them a small quantity of the reagent and allowing them to stand.

5. A reduction of barium sulphate to the sulphide may be caused by the reducing action of the burning carbon of the filter, but subsequent ignition, with ready access of air, reconverts the sulphide to sulphate, unless a considerable reduction has occurred. In the latter case it is expedient to add one or two drops of sulphuric acid, and to heat cautiously until the excess of acid is expelled.

6. Most impurities which are inclosed by the sulphate

cannot be removed by washing with water; treatment with hydrochloric acid, even if it accomplishes the removal of these impurities, dissolves some of the sulphate, which must be recovered. It is advisable, then, in any case, and essential when the contamination is due to iron, alumina, or silica, to purify by fusion with sodium carbonate, as described in the procedure. By this process the impurities are either rendered insoluble, and are removed by filtration with the barium carbonate, or, if they pass into solution with the sodium sulphate, they are present in such small amounts relatively, that they fail to be carried down by a second precipitation of the sulphate. It is obvious that the excess of alkaline carbonate must be destroyed by hydrochloric acid, and that the same care must be taken in the addition of the barium chloride the second time, as was taken at first. The reaction during fusion is the following:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
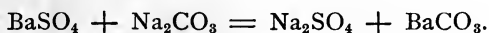
7. The removal of the fused mass from the crucible is facilitated by the procedure outlined, because, after the second short heating, the crucible, by its more rapid cooling, springs away from the mass inside. The boiling with water is sometimes necessary to dissolve a slight ring of carbonate, which solders the mass to the crucible at its upper edge.

For a further statement of the properties of barium sulphate, the student is referred to *Fresenius' Quantitative Analysis*, under " Forms."

DETERMINATION OF PHOSPHORIC ANHYDRIDE IN APATITE.

The sample of apatite selected for analysis should be as nearly pure as possible. Specimens of the mineral which leave but a slight siliceous residue are not difficult to secure.

Procedure. — Grind the mineral in an agate mortar until no grit is perceptible. Transfer the substance to a weighing tube, and weigh out two portions, not exceeding 0.20 gram each, into two No. 2 lipped beakers. Pour over them 20 cc. of nitric acid (sp. gr. 1.2), and warm gently until solvent action has apparently ceased. Unless the absence of soluble silicates is assured, evaporate the solution cautiously to dryness, heat the residue, for about two hours, to 130° C., and treat it again with nitric acid, as described above; separate the residue of silica by filtration on a small filter (7 cm.) and wash with warm water, using as little as possible (see p. 15). Receive the filtrate in a No. 3 or No. 4 lipped beaker. Test the washings with ammonia for calcium phosphate, but add all such tests, in which a precipitate appears, to the original filtrate. The filtrate and washings should not exceed 100 cc. in volume. Add aqueous ammonia until the precipitate of calcium phosphate first produced just fails to redissolve, and then add a few drops of nitric acid until this is again brought into solution. Warm the solution until it cannot be comfortably held in the hand, and, after removal from the lamp, add 75 cc. of ammonium molybdate solution (68 grams MoO_3 per liter), which has been *gently* warmed, but which must be perfectly clear. Allow the mixture to stand at a temperature of about 50° to 60° C. for twelve hours. Filter off the yellow precipitate on an 9 cm. filter, and wash by decantation with a solution of ammonium nitrate made acid with nitric acid.* Allow the precipitate to remain in the beaker as far as possible. Test the washings for calcium with ammonia and ammonium oxalate.

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* This solution is prepared as follows: Mix 100 cc. of ammonia solution (sp. gr. 0.96) with 325 cc. of nitric acid (sp. gr. 1.2), and dilute with 100 cc. of water.

Add 10 cc. of molybdate solution to the filtrate, and leave it for a few hours. It should then be carefully examined for a *yellow* precipitate; a white precipitate may be neglected. The filtrate should not be thrown away, but should be placed in a suitable receptacle for "molybdenum residues," from which the molybdic acid may be recovered.

Dissolve the precipitate upon the filter, by pouring through it dilute aqueous ammonia (one volume of ammonia (sp. gr. 0.96) and three volumes water, which should be *carefully measured*), and receive the solution in the beaker containing the bulk of the precipitate. The total volume of filtrate and washings must not exceed 100 cc.

Calculate the volume of magnesium ammonium chloride solution ("magnesia mixture") required to throw out the phosphoric acid, assuming 40 per cent. P_2O_5 in the apatite. Measure out not more than 2 cc. in excess, and add this quantity to the cold ammoniacal solution, by dropping it from a glass tube, stirring the solution constantly. The rate of addition must not be greater than 10 cc. in a minute. Continue the stirring for a few moments, and set the solution aside, at the temperature of the laboratory, over night. (Or it may be stirred constantly for a half-hour, when the precipitation should be complete.) The magnesium ammonium phosphate is then removed by filtration and washed with a mixture of one part ammonia (sp. gr. 0.96), one part alcohol, and three parts water, until 3 cc. of the washings show no evidence of chlorides. The washings must be acidified with nitric acid before the silver nitrate is added. Test the filtrate carefully for complete precipitation by adding more magnesia mixture and allowing it to stand.

Cover the funnel with a paper, dry the filter completely in the drying closet, and then ignite, using great care to insure the presence of plenty of oxygen during the combustion of the filter paper, thus guarding against a possible reduction of the phosphate, with disastrous consequences both to crucible and analysis. Do not raise the temperature above moderate redness until the precipitate is *white*. (Keep this precaution well in mind.) Ignite finally at the

highest temperature of the Tirrill burner, and repeat the heating until the weight is constant. From the weight of magnesium pyrophosphate ($Mg_2P_2O_7$) obtained, calculate the weight of phosphoric anhydride (P_2O_5), and the percentage of the latter in the sample of apatite.

Notes.— 1. Apatite may contain, beside calcium phosphate, either calcium fluoride or chloride. It is evident that the direct precipitation of the phosphoric acid in combination with magnesium is impracticable in the presence of any metal which forms compounds with phosphoric acid which are insoluble in ammoniacal liquids; such, for example, as iron, aluminum, chromium, and the alkaline earths. The previous isolation of the phosphoric acid in combination with molybdenum, which can be effected in nitric acid solution, is then necessary. The phospho-molybdate is soluble in ammonia, and from this solution the phosphoric acid may be separated as magnesium ammonium phosphate.

2. As a result of the slight solubility of magnesium ammonium phosphate, as noted below, the unavoidable errors of analysis are greater in this determination than in those which have preceded it, and some divergence may be expected in duplicate analyses. It is obvious that the larger the amount of substance taken for analysis, the less will be the relative loss or gain due to experimental errors; but in this instance a check is placed upon the amount of material which may be taken, both by the bulk of the resulting precipitate of ammonium phospho-molybdate, and by the excessive amount of ammonium molybdate required to effect complete separation of the phosphoric acid, since a liberal excess above the theoretical quantity is demanded. Molybdic acid is one of the more expensive reagents.

3. Soluble silicic acid might, if present, partially separate with the phospho-molybdate, although not in combination with molybdenum. Its previous removal by dehydration is therefore advisable.

4. Nitric acid is chosen as a solvent because the phospho-molybdate is slightly soluble in hydrochloric acid. An excess of nitric acid also exerts a slight solvent action, while ammonium nitrate lessens the solubility; hence the neutralization of the former by ammonia.

5. The composition of the " yellow precipitate " undoubtedly varies slightly with varying conditions at the time of its formation, and on this account the precipitate is not commonly separated and weighed as such. Its structure may probably be répresented by the symbol, $(NH_4)_3PO_4. 12 MoO_3. H_2O$, when precipitated under the conditions prescribed in the procedure. Whatever other variations may occur in its composition, the ratio of $12 MoO_3 : 1 P$ seems to hold, and this fact is utilized in volumetric processes for the determination of phosphorus, in which the molybdenum is reduced to a lower oxide and re-oxidized by a standard solution of potassium permanganate.

6. The precipitation of the phospho-molybdate takes place more promptly in warm than in cold solutions, but the temperature should not exceed $60°$ C. during precipitation ; a higher temperature tends to separate molybdic acid from the solution. This acid is nearly white, and its deposition in the filtrate on long standing should not be mistaken for a second precipitation of the yellow precipitate.

The addition of 75 cc. of ammonium molybdate solution insures the presence of a liberal excess of the reagent.

7. When washing the siliceous residue, the filtrate may be tested for calcium by adding ammonia alone, since that reagent neutralizes the acid which holds the calcium phosphate in solution and causes precipitation ; but after the removal of the phosphoric acid in combination with the molybdenum, the addition of an oxalate is required to show the presence of calcium.

8. Magnesium ammonium phosphate is not a wholly insoluble body, even under the most favorable analytical conditions. It is least soluble in a liquid containing one fourth of its volume of aqueous ammonia (sp. gr. 0.96), and this proportion should be carefully preserved, as prescribed in the procedure. On account of this slight solubility, the volume of solutions should be kept as small as possible, and the amount of wash-water limited to that absolutely required. The addition of alcohol to the wash-water lessens the solubility of the magnesium compound in it.

9. A large excess of the magnesium solution tends both to throw out magnesium hydroxide (shown by a flocculent precipitate), and to cause the phosphate to carry down molybdic

acid. The latter, if its presence be suspected, may be removed from the phosphate by dissolving the precipitate in hydrochloric acid, and passing sulphuretted hydrogen through the warm solution from three to four hours.

The tendency of the magnesium precipitate to carry down molybdic acid is greater if the solution is too concentrated. The volume should not be less than 90 cc. nor more than 125 cc. at the time of precipitation with the magnesia mixture.

10. The magnesium ammonium phosphate should be perfectly crystalline, and will be so if the directions are followed. The slow addition of the reagent is essential, and the stirring not less so. Stirring promotes the separation of the precipitate and the formation of larger crystals, and may therefore be substituted for digestion in the cold. The stirring rod must not be allowed to scratch the glass, as the crystals adhere to such scratches and are removed with difficulty.

The remarks on page 12, regarding the formation of large crystals by digestion with the solution, have peculiar force in connection with the magnesium ammonium phosphate, which is a *relatively* soluble body.

11. During ignition, the magnesium ammonium phosphate loses ammonia and water, and is converted into magnesium pyrophosphate.

$$2\ NH_4MgPO_4 = Mg_2P_2O_7 + 2\ NH_3 + H_2O.$$
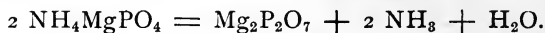
The precautions mentioned on page 16 must be observed with great care during the ignition of this precipitate. The danger here lies in a possible reduction of the phosphate. The phosphorus then attacks and injures the crucible, and the determination is valueless.

If extreme care is employed, it is possible to safely ignite this precipitate without previous drying, but the student is not advised to attempt this until some general experience has been gained.

For a further statement of the properties of ammonium phospho-molybdate, magnesium ammonium phosphate, and magnesium pyrophosphate, the student is referred to *Fresenius' Quantitative Analysis*, under " Forms."

DETERMINATION OF CALCIUM, MAGNESIUM, AND CARBON DIOXIDE IN DOLOMITE.

The sample of dolomite chosen for practice should leave little or no residue insoluble in hydrochloric acid.

DETERMINATION OF CALCIUM.

Procedure. — Grind the mineral to a fine powder. Weigh out, into 150 cc. casseroles, two portions (*a* and *b*) of about one gram each. Pour over them 30 cc. of hydrochloric acid (sp. gr. 1.12), first having covered the casseroles ; add 1 cc. of nitric acid (sp. gr. 1.20) and boil five minutes. Filter off the residue on a small filter, wash five times with hot water, and ignite the filter in a platinum crucible. Cover the filter ash and residue with a *small quantity* (perhaps 0.5 gram) of sodium carbonate, heat to fusion, and disintegrate with a little water, by cautiously boiling it in the crucible. Add this solution, with any suspended matter, to the main filtrate from the insoluble residue ; evaporate the solution to dry-ness, and heat the residue in the hot closet for two hours at 130° C., to dehydrate any soluble silicic acid. Moisten the residue with hydrochloric acid, warm gently, dilute to 100 cc., and bring to boiling. Add 5 cc. of ammonium chloride solution, aqueous ammonia in slight excess, and, if manganese is present, add 5 cc. of bromine water and boil for five minutes, adding more ammonia, if need be. If man-ganese is absent, omit the bromine. In either case, finally neutralize the excess of ammonia until a faint odor only can be detected, and filter off the silicic anhydride, together with the iron, aluminum, and manganese hydroxides. The filtration must take place promptly after the addition of the ammonia. Without washing the precipitate, re-dissolve it on the filter in hydrochloric acid, receiving the solution in a clean beaker. Wash the filter five times with water, and throw down the hydroxides from the solution as before. Wash this precipitate with hot water until free from chlo-rides. The precipitate may then be discarded.

Treat the combined filtrates from portion (*a*) as follows : To the filtrate, concentrated to 250 cc. and heated to boiling,

add ammonium oxalate solution in moderate excess, stirring well, and adding the reagent slowly. Boil for two minutes, allow the precipitated calcium oxalate to settle for a half-hour, and decant through a filter. Test the filtrate for complete precipitation by adding a few drops of the precipitant. If no precipitate forms, make the solution slightly acid with hydrochloric acid, and proceed with the magnesium determination.

Re-dissolve the calcium oxalate in the beaker, and from the filter, with hydrochloric acid, washing the filter five times, and finally pouring through it aqueous ammonia. Dilute the solution to 250 cc., bring to boiling, add 1 cc. ammonium oxalate solution and ammonia in slight excess; boil for two minutes, and set aside for a half-hour. Filter off the calcium oxalate upon the filter first used, and wash free from chlorides. The filtrate should be made barely acid and combined with the first filtrate.

The precipitate of calcium oxalate may be ignited without drying. It should be ignited at the highest heat of the Bunsen or Tirrill burner, after destroying the filter, and finally for three minutes at the blast lamp. Repeat until the weight is constant. As the calcium oxide absorbs moisture from the air, it must be weighed as rapidly as possible. (Compare Note 7, on p. 31.) From the weight of the oxide calculate the weight of calcium, and the percentage of the latter in the dolomite.

Treat the combined filtrates from the iron precipitates (*b*) as follows: Add hydrochloric acid to decided acid reaction. Calculate the volume of ammonium oxalate solution required to combine with both the calcium and magnesium, assuming the presence of 20 per cent. of each. Add this volume to the solution and, if a precipitate forms, dissolve it in hydrochloric acid. Dilute the whole to 1000 cc. and bring it to boiling. Remove it from the hot plate and slowly add ammonia in moderate excess, with constant stirring. Allow the solution to stand for a half-hour, filter off the calcium oxalate, and wash the precipitate with hot water until freed from chlorides. Ignite this precipitate as described in procedure (*a*).

Barely acidify the filtrate from the calcium oxalate with

hydrochloric acid, and proceed with the magnesium determination.

DETERMINATION OF MAGNESIUM.

Procedure. — Evaporate the acidified filtrates from the cal-cium precipitates until salts begin to crystallize, but do not evaporate to dryness. Dilute until these salts are brought into solution. Add a volume of aqueous ammonia (sp. gr. 0.96) equal to one third the volume of the solution. (To do this, measure into a beaker of equal size a volume of water equal to the volume of the solution. Note the number of cubic centimeters and take one third as many of ammonia.) Calculate the volume of hydrogen sodium phosphate solution required to precipitate the magnesium, assuming 20 per cent. to be present. Add the sodium phosphate to the cold solution drop by drop from a glass tube, at a rate not greater than 10 cc. per minute; stir thoroughly, set aside for some hours, and treat the precipitate of magnesium ammonium phosphate as prescribed for the determination of phosphoric anhydride, on page 37.

> *Notes.* — 1. The mineral Dolomite is a native isomorphous mixture of calcium and magnesium carbonates, in which the relative proportions may vary widely. Ferrous iron and manganese are not infrequently present, and most specimens leave a larger or smaller residue on treatment with hydrochloric acid. Since this residue may contain calcium or magnesium, it must be rendered soluble by fluxing, and brought into solution. This may be quickly accomplished, if the directions are closely followed with regard to the use of a small quantity of the sodium carbonate and disintegration of the small fused mass within the crucible.
>
> If it is definitely known, from a qualitative examination, that the residue insoluble in hydrochloric acid contains no calcium or magnesium, its treatment may be omitted, and the solution may be at once evaporated for the dehydration of the silica, without filtration. The insoluble residue may be filtered off with the hydroxide precipitate.
>
> 2. The addition of nitric acid is necessary to oxidize ferrous iron to ferric, and to insure its complete precipitation by

ammonia. Manganese is not oxidized by nitric acid, but is oxidized by bromine in ammoniacal solution to a hydrated dioxide, in which form it is precipitated and removed with the iron and alumina. The possible presence of alumina makes it necessary to finally neutralize all but a slight excess of ammonia before filtration. (Compare Note 8, p. 31.)

3. The iron precipitate should be filtered off promptly, since the alkaline solution absorbs carbon dioxide from the air, with consequent precipitation of the calcium as carbonate. This is possible even under the most favorable conditions, and for this reason the iron precipitate is re-dissolved and thrown out again, to free it from calcium.

4. The separation of calcium and magnesium as oxalates requires special precautions. It is necessary either to re-dissolve the first precipitate of calcium oxalate, and make a second precipitation, as in procedure (*a*), or to separate in dilute solution and in the presence of sufficient ammonium oxalate to combine with both metals, as in procedure (*b*). In (*a*), the first calcium precipitate contains magnesium, but when dissolved, the proportion of magnesium to the calcium in solution is small, and the second calcium precipitate may be considered to be pure. In (*b*), it is sought to accomplish the same end by liberal dilution in the presence of an excess of ammonium oxalate, lessening in this way the tendency of the magnesium to separate with the calcium. Method (*a*) probably yields results which are more certainly accurate than (*b*), for large amounts of the two metals, while (*b*) is accurate for small quantities.

5. The small quantity of ammonium oxalate solution is added before the second precipitation of the calcium oxalate, to insure the presence of a slight excess of the reagent, which promotes the separation of the calcium compound.

6. On ignition the calcium oxalate loses carbon dioxide and carbon monoxide, leaving calcium oxide.

$$CaC_2O_4 = CaO + CO_2 + CO.$$
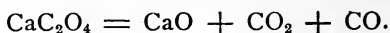
For small weights of the oxalate (0.5 gram or less), this reaction may be brought about at the highest temperature of a Tirrill burner, but it is well to ignite larger quantities than this over the blast lamp until the weight is constant.

7. The calcium oxide tends to absorb moisture to form the hydroxide; hence the necessity for rapid weighing.

8. The filtrate from the calcium oxalate should be made slightly acid immediately after filtration, in order to avoid the solvent action of the alkaline liquid upon the glass.

9. The precipitation of the magnesium should be made in as small volume as possible, and the ratio of ammonia to the total volume of solution should be carefully provided for, on account of the slight solubility of the magnesium ammonium phosphate. This matter has been fully discussed in connection with the phosphoric anhydride determination. (Compare Note 8, p. 39.)

10. If the magnesium ammonium phosphate precipitate is not wholly crystalline, as it should be, the difficulty may sometimes be remedied by filtering the precipitate and, without washing it, re-dissolving in a small quantity of hydrochloric acid, from which it may be again thrown down by ammonia, after adding a few drops of sodium phosphate solution. If the flocculent character was occasioned by the presence of magnesium hydroxide, the second precipitation, in a smaller volume, containing fewer salts, will often result more favorably. The removal of iron or alumina from a contaminated precipitate is a matter involving a long procedure, and a re-determination of the magnesium from a new sample, with additional precautions, is usually to be preferred.

For a further statement of the properties of calcium oxalate and calcium oxide, the student is referred to *Fresenius' Quantitative Analysis*, under " Forms."

DETERMINATION OF CARBON DIOXIDE.

The apparatus required for the determination of the carbon dioxide should be previously arranged as shown in the cut on page 46. The flask *A* is arranged as an ordinary wash bottle, in which should be placed 50 cc. of hydrochloric acid (sp. gr. 1.12) and 100 cc. of water. This flask is connected by rubber tubing with the tube (*b*) leading nearly to the bottom of the evolution flask (*B*) and having its lower end bent upward to avoid loss of gas   The evolution flask may conveniently be a wide-mouthed Soxhlet extraction flask of about 150 cc. capacity, the mouth of which is fitted with a double-bored rubber stopper. *C* is a ball-condenser (or may be a small glass [Liebig] condenser), from the top of which

a delivery tube leads to the U-tube (D), containing some glass beads and 3 cc. of a saturated solution of silver sulphate with 3 cc. of concentrated sulphuric acid. The second tube (E) is filled with calcium chloride, and should have a small, loose plug of cotton at the top of each arm. Both tubes should be closed by cork stoppers, the tops of which are sunk slightly below the top of the U-tube, and then neatly sealed with sealing wax.

The Geissler bulb (F) should be so filled with potassium hydroxide solution (sp. gr. 1.27) that each small bulb is about two thirds full. There should be attached to the bulb, in such a manner that it can be weighed with it, a filled calcium chloride tube (3 in.). A platinum wire should be attached to the bulb to permit it to hang upon the support.

An additional U-tube, to be used as a safety tube (H), should be filled with soda-lime ready for use.
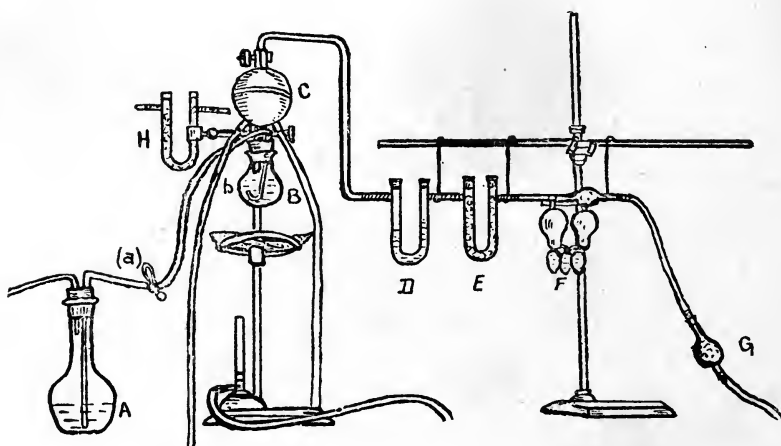
When the apparatus is ready, weigh out into the flask (B) about 0.8 gram of the dolomite and cover it with 15 cc. of water. Carefully wipe the Geissler bulb (F), with its calcium chloride prolong tube, and weigh accurately. Afterward stopper the openings by means of small pieces of rubber tubing closed by pieces of glass rod.

Place the flask (*B*) on the apparatus, making sure that the stopper fits tightly, and connect the Geissler bulb with the U-tubes; disconnect the rubber tube from *A*, close the pinch-cock (*a*), apply suction at the end of the Geissler bulb, and note whether the apparatus is absolutely air-tight. This precaution must not be neglected, and care must afterward be taken to admit air slowly, by cautiously opening (*a*), to equalize the pressure. The rubber tube must, of course, contain no hydrochloric acid at this time.

When it is certain that the apparatus is ready for use, connect the rubber tube with the flask (*A*), and, opening the pinch-cock (*a*), blow over about 10 cc. of the diluted acid. When the evolution of carbon dioxide slackens add a fresh portion of acid. The gas should not enter the Geissler bulb more rapidly than two bubbles per second. When the action of the acid ceases in the cold, run water through the condenser (*C*) and apply a small flame to the flask, cautiously bringing the liquid to the boiling point, and continue to boil it slowly for about three minutes. Replace the flask (*A*) by the safety tube (*H*). Apply suction at the end of the Geissler bulb, and regulate it in such a way that when the pinch-cock (*a*) is opened the air will pass slowly through the apparatus, the rate not to exceed that named above. Do not remove the lamp from under the flask (*B*) until the air current is adjusted. Continue to draw air through the apparatus from twenty to thirty minutes; then disconnect the Geissler bulb, stopper it, place it in the balance room, and, after an interval of thirty minutes, wipe it carefully, and weigh it without the stoppers. The increase in weight is due to absorption of carbon dioxide. Repeat the determination with a fresh portion of dolomite.

Notes. — 1. By very cautious procedure it is possible to avoid the use of a condenser above the evolution flask, or, a tube with one or two bulbs blown in it may be substituted. More moisture is then likely to be carried over into the U-tubes, which soon require refilling.

2. The air current may conceivably carry minute quantities of hydrochloric acid through the apparatus. This acid

would be retained by the silver sulphate solution in the first
U-tube. The beads serve to divide the bubbles of gas as
they pass through the liquid. The sulphuric acid lessens the
evaporation of the silver sulphate solution.

The calcium chloride in the second tube assures the re-
moval of the water from the moisture-laden air from the
evolution flask. As calcium chloride frequently contains
basic salts which would retain carbon dioxide, it is neces-
sary to pass a current of that gas through the U-tube for a
short time, and follow this by a current of dry air for thirty
minutes before using the tube.

3. The potassium hydroxide unites with the carbon di-
oxide to form potassium carbonate. The hydroxide must be
present as a concentrated solution to insure complete absorp-
tion, and to avoid a loss of water with the air which passes
through the bulbs. The small quantity of moisture which is
taken up by the air is retained by the calcium chloride of
the prolong tube. The best form of Geissler bulb is that
to which the calcium chloride prolong is attached by a
ground-glass joint.

5. Carbon dioxide is dissolved by cold water, but the gas
is expelled by boiling. This residual volume of gas, together
with that which is distributed through the apparatus, is swept
out through the absorption bulb by the current of air. This
is purified by drawing it through the tube (H) containing
soda-lime, which removes any carbon dioxide which may be
in the atmosphere.

6. Instead of the potassium hydroxide in a Geissler bulb,
soda-lime, which should be placed in two U-tubes with suit-
able device for weighing, may be employed to absorb the
carbon dioxide. Soda-lime is a mixture of sodium and cal-
cium hydroxides, and unites with the gas to form carbonates.
Some care is necessary to guard against loss of moisture from
the soda-lime, as considerable heat is generated during the
absorption.

7. With Geissler bulbs of the usual size two determina-
tions may be safely made without refilling the bulbs. A
precipitate of acid potassium carbonate in the first of the
bulbs is an evidence that the absorbing power of the hydrox-
ide is nearly exhausted.

8. Great care is necessary when the suction is applied to

avoid a violent passage of gas through the apparatus and to prevent regurgitation.

It is advisable to interpose a tube (G) containing calcium chloride and soda-lime between the suction tube and the potash bulb to prevent possible contamination.

9. The large surface presented to the air by the Geissler bulbs admits of the accumulation of dust and moisture during the determination. They must, therefore, be cautiously cleaned before each weighing, by wiping with a clean, lintless cloth, or a piece of wash-leather. They should stand for thirty minutes near the balance to assure uniformity of temperature, any change of which at the second weighing of so large a weight might cause an appreciable error.

The stoppers should be removed from the bulbs on weighing, that the air inclosed may be at atmospheric pressure.

10. A large number of procedures have been proposed for the determination of carbon dioxide by loss of weight, but most of these require special forms of apparatus. Descriptions of such processes can be found in any large work on quantitative analysis.

3 weeks

DETERMINATION OF LEAD, COPPER, AND ZINC IN BRASS.

DETERMINATION OF LEAD.

Procedure. — Select clean, bright chips or borings, or, if the brass is in the form of wire, polish a piece of suitable size by rubbing with emery, cleaning it carefully afterward. Weigh out two portions of about 5 grams each, and dissolve them in covered casseroles in 30 cc. of nitric acid (sp. gr. 1.2). When the solution is complete, cool, wash off the cover glass, and add slowly 10 cc. of sulphuric acid (sp. gr. 1.84). Evaporate under a hood until heavy white fumes of sulphuric anhydride are evolved, keeping the casserole well covered meanwhile ; cool, add 125 cc. of water, and boil until the sulphates of copper and zinc have dissolved, and set the solution aside until perfectly cold. Filter off the lead sulphate, wash it by decantation with dilute sulphuric acid (one volume of concentrated acid to twenty volumes of water) until the washings are free from copper, as shown by the ammonia test. Set the filtrate aside for the determination of copper and zinc, and transfer the lead sulphate to the filter, finally washing the filter free from sulphuric acid, with alcohol diluted with an equal volume of water. Be sure that all the sulphate is removed from the casserole. Discard the alcoholic washings, if they are entirely clear. Dry the filter, and, if practicable, separate the lead sulphate from it, as described on page 24. Prepare a No. 7 porcelain crucible for use, by heating and weighing, burn the filter on a platinum wire, as described on page 24, and when cold, add to the ash two drops of nitric acid and one drop of sulphuric acid. Ignite with great care until the acids are expelled. Transfer the precipitate which was separated from the filter, to the crucible, and ignite at a moderate red heat. Repeat the heating until the weight is constant.

From the weight of the lead sulphate, calculate the weight of lead, and the percentage of the latter in the brass.

Notes. — 1. It is obvious that the brass taken for analysis should be untarnished, which can be easily assured when wire is used, by scouring with emery. If chips or borings are used, they should be well mixed, and the sample for analysis taken from different parts of the mixture.

2. The small percentage of lead usually found in brasses makes it necessary to weigh out a considerable quantity in order to secure accuracy. The amount taken, 5 grams, is too large to use directly for the determination of copper and zinc, on account of the bulk of the precipitates which would then have to be handled. An aliquot part of this filtrate is, there-fore, used for these analyses, as noted under the determination of copper.

3. Lead sulphate is slightly soluble in nitric acid; hence the latter is removed by heating with sulphuric acid until the more volatile acid is expelled. This point is indicated by the appearance of the heavy, white fumes.

4. Lead sulphate is least soluble in dilute sulphuric acid (1 : 20). The sulphuric acid solution is, therefore, diluted to secure this ratio, and a wash-water of the same strength is used.

The sulphuric acid of the wash-water, if allowed to remain on the filter, would char it during the drying, making subsequent handling difficult or impossible. It is accordingly removed by washing with dilute alcohol; but the alcohol is not added to the main filtrate, as its presence is not advantageous during the subsequent operations.

5. The lead sulphate must be separated from the filter for the same reasons which apply in the case of silver chloride. (Compare p. 26.) The addition of nitric acid to the ash dissolves any reduced lead, and the sulphuric acid converts it to sulphate. A slight loss of lead is possible if the reduction of any considerable quantity of the precipitate takes place, and it is evident that the ignition of this precipitate in platinum is impracticable.

6. It is possible to determine the percentage of lead in the brass by solution in nitric acid, partial neutralization of the excess of acid, and deposition of the lead by an electric current as peroxide (PbO_2) on the anode; but the relatively large percentage of copper makes the simultaneous determination of that element difficult, if a sufficiently large quan-

tity of the brass be taken for analysis to also secure an accurate determination of the lead. For the determination of small quantities of lead alone, this method might be employed.

For a further statement of the properties of lead sulphate, the student is referred to *Fresenius' Quantitative Analysis,* under " Forms."

DETERMINATION OF COPPER.

Procedure.— Transfer the filtrate from the lead sulphate to a 500 cc. graduated flask, washing out the beaker carefully. Fill the flask with distilled water until the lowest point of the meniscus is exactly level with the mark on the neck of the flask. Carefully remove, with a strip of filter paper, any drops of water which are on the inside of the neck of the flask above the graduation; make the solution thoroughly uniform by pouring it out into a *dry* beaker, and back into the flask several times, and finally stopper the flask. Measure off one tenth of this solution as follows: Pour into a 50 cc. graduated flask about 10 cc. of the solution, shake the liquid thoroughly over the inner surface of the small flask and pour it out. Repeat the same operation. Fill the 50 cc. flask until the lowest point of the meniscus is exactly level with the mark on its neck, remove any drops of solution from the upper part of the neck with filter paper, and pour the solution into a plain beaker of about 80 cc. capacity, of rather tall form. Wash out the flask with small quantities of water until it is clean, adding these to the main solution. (Consult also note on p. 72.) When the second portion of 50 cc. is measured out, remember that the flask must be twice rinsed out with solution as prescribed above, before the final measurement is made.

Add to the copper solution 1 gram of ammonium nitrate. The solution is then ready for the electrolytic deposition of the copper.

Meanwhile, four platinum electrodes, two anodes and two cathodes, should be cleaned by scouring with sapolio and treatment with acid, and the two cathodes ignited gently and cooled in a desiccator. Weigh them carefully, and place one anode and one cathode in each solution. The connections

should then be made with the binding posts (or other device for connection with the electric circuit), in such a way that the copper will be deposited upon the larger electrode. If a gravity battery is used, this electrode should be connected with the zinc pole; if a dynamo-current is used, a previous qualitative experiment is necessary to determine the negative pole. Subject the solution to the action of the current from eight to fifteen hours, as indicated by the rate of deposition. It is well to leave the solution over night, if practicable.

When the solution is colorless, and the deposition of copper seems to be complete, break the circuit as follows : Lift the cathode in the binding post until it is nearly, but not wholly, out of the liquid, and wash the exposed portion with distilled water. Then break the circuit by removing the electrode entirely, and complete the washing promptly. Pour over the electrode and copper enough alcohol to remove adhering water, and dry for a few moments at 105° C. Cool in a desiccator and weigh. Test the solution for copper by the addition of ammonia in excess, to about 5 cc. of the solution. If copper is found, clean the electrodes and place the solution in the circuit a second time. Whether copper is found or not, return the test portion to the main solution.

The increase in weight of the electrode represents directly the weight of copper from one tenth of the solution, from which the percentage in the brass may be calculated.

Notes. — 1. The removal of one tenth of the solution for the determination of copper and zinc is necessitated by the difficulties which would be encountered if the precipitation of such large quantities of these metals as would come from 5 grams of the brass, was attempted. The solution is, therefore, diluted to a definite volume (500 cc.), and exactly one tenth (50 cc.) is measured off. To attain this end it is evident that the solution must be thoroughly uniform, which is brought about by careful mixing, and that it must not be diluted by water adhering to the small flask. This is insured by rinsing out this flask several times with the solution, instead of drying it, which would consume much time. The two flasks must be graduated at the same temperature,

and if, as is usual, the small flask is graduated to *contain* 50 cc., it must be rinsed out with water before all the copper and zinc belonging to one tenth of the solution are obtained. This, and other kindred considerations, are discussed under Volumetric Analysis, page 72. A pipette might properly be substituted for the small flask, if desired.

2. The presence of sufficient ammonium nitrate to react with the sulphuric acid in the solution, lessens the tendency of the copper to deposit on the cathode in a spongy condition. The amount of the nitrate added should not greatly exceed 1 gram.

3. The electrodes should be freed from all greasy matter before using, and after scouring, those portions upon which the metal will deposit should not be touched with the fingers.

4. Under the conditions named in the procedure, the copper may be deposited in satisfactory condition by a current from three cells of a "gravity battery," in series, or by the current which passes through three 10-candle Edison lamps, in series, on a 110-volt circuit. The deposition is usually complete after twelve to fifteen hours.

It is not well to leave the solution in the circuit for an excessive length of time, since, after the deposition of the copper, the nitric acid is slowly reduced to ammonia by the nascent hydrogen, with the possible production of an alkaline solution from which zinc may be thrown down.

5. The electrodes should be washed as far as possible before the current is broken, to prevent re-solution of the copper. If several solutions are connected in the same circuit, some provision must be made by which the breaking of the current shall be avoided when the electrodes in any one solution are removed. This can be easily accomplished by springing a piece of brass between the binding posts, before removing the electrodes. The current at first passes through both spring and solution, and when the current is broken in the latter, it passes through the spring instead, and no copper is dissolved from the electrodes in other solutions.

6. The electrode is washed with alcohol to promote rapidity of drying. The copper should not remain in the hot closet a moment longer than is necessary, as it tends to oxidize at the higher temperature.

7. A dark deposit on the anode indicates a precipitation

of lead as peroxide. Such deposition is not infrequent, as the lead sulphate is not absolutely insoluble in the acid liquid from which it separates. This electrode may be weighed with the precipitate, then cleansed and again weighed, and the amount of lead calculated from the weight of the peroxide added to that found as sulphate in the corresponding solution.

For a further statement of the properties of copper and of lead peroxide, the student is referred to *Fresenius' Quantitative Analysis*, under "Forms.'

DETERMINATION OF ZINC.

Procedure. — Transfer the solution, from which the copper has been removed, to large porcelain casseroles and dilute to 300 cc. Cover these casseroles and add sodium carbonate solution to distinctly alkaline reaction; boil until no odor of ammonia can be detected from the hot solution, adding water to replace loss by evaporation. Again add 1 cc. or 2 cc. of the sodium carbonate solution and boil to insure complete removal of the ammonia. Filter off the basic zinc carbonate, using two filters for each determination, if the precipitate is too bulky to be properly held by one; wash the precipitates three times by decantation with hot water, and finally on the filter until freed from carbonate.

Test the filtrate and washings for complete precipitation by the addition of a few drops of ammonium sulphide, and allow it to stand; if zinc sulphide separates, collect it on a filter, wash with water containing a very little ammonium sulphide, ignite in a porcelain crucible, and weigh as oxide.

Dry the precipitated basic carbonate in the drying closet, and separate the carbonate as completely as possible from the filter, as described on page 24. Clean, heat, and weigh a No. 7 porcelain crucible, burn the filter on a wire above it, allow the ash to fall into the crucible, and ignite until the carbon is all destroyed. Transfer the main portion of the precipitate to the crucible and ignite at a red heat, until the weight is constant. From the weight of zinc oxide, calculate the weight of zinc and the percentage of the latter in the brass, remembering that but one tenth of the solution was used for this determination.

Notes. — 1. Porcelain or platinum vessels are required when strongly alkaline solutions are to be boiled, as in this determination, to prevent the introduction of silica from the glass into the solution.

2. Sodium carbonate throws down a basic zinc carbonate, the exact composition of which probably varies with varying conditions. This precipitate is partially soluble in the presence of either ammonia or ammonium salts, and in the presence of carbon dioxide. Both of these may be removed by continued boiling with an excess of sodium carbonate.

The precipitate is frequently very voluminous, though it varies widely in this respect under apparently similar conditions. The student is therefore not to suppose that errors have been made if one precipitate should appear much larger than the other.

3. The filtrate should always be tested for zinc by the addition of ammonium sulphide; but when the boiling before filtration is sufficiently prolonged, no weighable quantity of zinc should be found in the filtrate. The zinc sulphide, if any appears, must be washed with water containing ammonium sulphide to prevent oxidation.

4. The basic zinc carbonate loses water and carbon dioxide on ignition, leaving the zinc oxide. This oxide may be reduced to metallic zinc by contact with burning carbon, and the zinc may volatilize; a separation of the main portion of the precipitate from the filter is, therefore, necessary. This separation should be made as complete as possible, without an admixture of shreds from the filter paper.

It is well to test the ignited zinc oxide, after weighing, with moist litmus paper for alkaline reaction. If this is found, the presence of alkali in the precipitate is indicated. It should then be boiled with water and again ignited, with the same precaution as before.

5. The zinc may also be determined in the solution from which the copper has been removed, by precipitation as zinc ammonium phosphate and ignition to pyrophosphate, a method preferred by many to the carbonate precipitation. For a description of this procedure the student is referred to *J. Soc. Chem. Ind.*, **15**, 866.

For a further statement of the properties of basic zinc carbonate and of zinc oxide, the student is referred to *Fresenius' Quantitative Analysis*, under " Forms."

DETERMINATION OF SILICA IN LAUMONTITE AND IN FELDSPAR.

Of the natural and artificially prepared silicates a comparatively few are completely decomposed by acids, while a large number require to be disintegrated by fusion before complete solution can be accomplished.

The mineral laumontite is taken as a type of the decomposable silicates, and feldspar of those requiring fusion for disintegration.

ANALYSIS OF LAUMONTITE.

Grind the mineral to a fine powder. Weigh out two portions of 0.5 to 0.6 gram each into 300 cc. porcelain casseroles. Pour over them 15 cc. of water, and stir until the powder is evenly mixed with the water. Add 25 cc. of hydrochloric acid (1.12 sp. gr.) in small portions, and warm until the mineral is wholly disintegrated, as indicated by a flocculent residue and absence of grittiness under the stirring rod (if any remains undissolved). Evaporate the solution to dryness, add 15 cc. of hydrochloric acid (sp. gr. 1.12), and again evaporate, and heat the residue for two hours at a temperature approximating 130° C. to dehydrate the silicic acid. Moisten the residue with hydrochloric acid (1.12 sp. gr.), warm gently, making sure that the acid comes into contact with the whole of the residue, dilute to 200 cc., and bring to boiling. Filter off the silica, wash four or five times with warm dilute hydrochloric acid (one part acid [1.12 sp. gr.] to three parts of water) and finally with hot water until free from hydrochloric acid. Transfer the filter to a platinum crucible and ignite, as described on page 16, to constant weight.

Cautiously pour into the crucible about 0.5 cc. of hydrofluoric acid. *This must be done in a hood, with a good draught, and great care must be taken that the acid does not come into contact with the hands, as it produces painful wounds.*

If the precipitate has dissolved in this quantity of acid, add two drops of concentrated sulphuric acid, and heat very slowly (always under the hood) until all the liquid has evaporated, finally igniting to redness. Cool in a desiccator, and weigh the residue. Deduct the weight of this residue from the previous apparent weight of silica, and from the difference calculate the percentage of silica present.

Notes. — 1. Laumontite is a hydrated silicate of aluminum and calcium. Other decomposable silicates or slags may be substituted for this mineral, as the procedure is of general application.

2. If strong acid were poured directly upon the powdered silicate a partial separation of gelatinous silicic acid would occur, and this jelly-like mass would inclose particles of the unchanged mineral protecting them from the action of the acid. The water is added to avoid this separation by distributing the particles and diluting the first portions of acid.

3. A flocculent residue will often remain after the decomposition of the mineral is effected. This is usually partially dehydrated silicic acid. Silicic acid is only completely held in solution by acids when it is in the fully hydrated condition, corresponding to the symbol $Si(OH)_4$. This compound is very unstable, and soon loses water, separating from solutions as the loss increases, until, on protracted heating at temperatures above $100°$ C., it loses all its water, and becomes practically insoluble. The progress of the dehydration is indicated by the behavior of the solution, which as evaporation proceeds usually gelatinizes. On this account it is necessary to allow the solution to evaporate on a steam bath, or to stir it vigorously, to avoid loss by spattering.

4. To obtain pure silica, the residue, after evaporation, must be thoroughly extracted by warming with hydrochloric acid, and the solution freely diluted to prevent, as far as possible, the inclosure of the residue in the particles of silica.

5. Aluminum and iron are likely to be thrown down as basic salts from hot, very dilute solutions of their chlorides If the silica were washed only with hot water, the solution of these chlorides remaining in the filter after the passage of the original filtrate, would gradually become so dilute as to throw

down basic salts within the pores of the filter, which would remain with the silica. To avoid this, an acid wash water is used until the aluminum and iron are practically removed. The acid is then removed by water.

6. The silica undergoes no change during the ignition beyond the removal of all traces of water.

7. Notwithstanding all precautions, the ignited precipitate of silica is rarely wholly pure. It is tested by volatilization of the silica as silicon fluoride after solution in hydrofluoric acid, and, if the analysis has been properly conducted, the residue, after treatment with the acids and ignition, should not exceed one milligram.

The acid produces ulceration if brought into contact with the skin, and its fumes are excessively harmful if inhaled.

8. The impurities are probably weighed with the original precipitate as oxides. The addition of the sulphuric acid displaces the hydrofluoric acid, and the resulting sulphates (usually of iron or aluminum) are converted to oxides by the final ignition.

It is obvious that unless the acids used are known to leave no residue on evaporation, a quantity equal to that employed in the analysis must be evaporated, and a correction applied for any residue found.

9. According to Gilbert (*Technology Quarterly*, 3, 61) it is frequently impracticable to render silicic acid completely insoluble by action of heat alone. The silica which passes into solution is thrown down on the addition of ammonia, with the iron and aluminum, and may be recovered by igniting this precipitate, grinding it carefully in an agate mortar, fusing it with acid potassium sulphate, dissolving the fused mass in water, and filtering off and weighing the silica.

The amount of silica which fails of determination by the heating alone, as prescribed above, is very small, and is, in this instance, lessened by the presence of calcium chloride from the laumontite itself. This additional procedure for the recovery of the soluble silica may be omitted unless extreme accuracy, as in certain mineral analyses, is essential.

For a further statement of the properties of silicic acid and of silica the student is referred to *Fresenius' Quantitative Analysis*, under "Forms."

ANALYSIS OF FELDSPAR.

Grind about 3 grams of the mineral in an agate mortar until no grittiness is to be detected when the mineral is placed between the teeth, or, better, until it will entirely pass through a sieve made of fine silk bolting cloth. The sieve may be made by placing a piece of the bolting cloth over the top of a small beaker in which the ground mineral is placed, holding the cloth in place by means of a rubber band below the lip of the beaker. By inverting the beaker over clean paper and gently tapping it, the fine particles pass through the sieve, leaving the coarser particles within the beaker. These must be returned to the mortar and ground until they will pass through the sieve.

Weigh out into platinum crucibles two portions of the ground feldspar of about 0.8 gram each. Weigh out on rough balances two portions of anhydrous sodium carbonate, each amounting to about six times the weight of the feldspar taken for analysis. Pour about three fourths of the sodium carbonate into the crucible, place the latter on a piece of clean, glazed paper, and thoroughly mix the substance and the flux by carefully stirring for several minutes with a dry glass rod. The rod may be wiped off with a small fragment of filter paper, which may be placed in the crucible. Place the remaining fourth of the carbonate on the top of the mixture. Cover the crucible, heat it to dull redness for five minutes, and then increase the heat to the full capacity of a Bunsen or Tirrill burner for twenty minutes, or until a quiet liquid fusion is obtained. Finally heat the sides and cover strongly, until any material which may have collected upon them is also brought to fusion.

Allow the crucible to cool, and remove the fused mass as directed on page 32. Disintegrate the fused mass by placing it in a previously prepared mixture of 100 cc. of water and 50 cc. of hydrochloric acid (sp. gr. 1.12), in a covered casserole. Clean the crucible and lid by means of a little hydrochloric acid, adding this acid to the main solution. When disintegration is complete, evaporate the solution to

dryness, heat the residue to 130° C. for two hours, and proceed as in the analysis of laumontite.

Notes. — 1. If the feldspar is in the massive or crystalline form, clean pieces should be selected, and crushed in an iron mortar to about half the size of a pea, and then transferred to a steel mortar, in which they are reduced to a coarse powder ready for the agate mortar. A wooden mallet should always be used to strike the pestle of the steel mortar, and the blows should not be sharp.

It is plain that the grinding must continue until the whole of the portion of the mineral originally taken has been ground so that it will pass the bolting cloth, otherwise the sifted portion does not represent an average sample, the softer ingredients, if foreign matter is present, being first reduced to powder. For this reason it is best to start with about the quantity of the feldspar needed. Any coarse particles remaining would resist the action of the flux.

2. During the fusion the feldspar, which is a strictly a silicate of aluminum and either sodium or potassium, but usually contains some iron, calcium, and magnesium, is decomposed by the alkaline flux, the sodium of the latter combining with the silicic acid of the silicate with the evolution of carbon dioxide, while about two-thirds of the aluminum forms sodium aluminate, and the remainder is converted to a basic carbonate, or the oxide. The calcium and magnesium, if present, are changed to carbonates, and, with the aluminum oxide, remain undissolved on treatment with water. The heat is applied gently, to prevent a too violent reaction at the start.

3. The silicic acid must be freed from its combination with a base (sodium, in this instance) before it can be dehydrated. The excess of hydrochloric acid accomplishes this liberation. By disintegrating the fused mass with a considerable volume of dilute acid the silicic acid is at first held in solution to a large extent, and on evaporation and re-solution of the bases, the silica is left in a better condition for filtration and washing. Immediate treatment of the fused mass with strong acid is likely to cause the silicic acid to separate at once, and to inclose alkali salts, or alumina.

4. A portion of the fused mass is usually projected up-

ward by the escaping carbon dioxide during the fusion. The crucible must therefore be kept covered as much as possible, and the lid carefully cleaned.

5. A gritty residue remaining after the disintegration of the fused mass by water indicates that the substance has been but imperfectly decomposed. Such a residue should be filtered, washed, dried, ignited, and again fused with the alkaline flux; or, if the quantity of material at hand will permit, it is better to reject the analysis, and to use increased care in grinding the mineral and in mixing it with the flux.

A large residue remaining after the volatilization of the silica also indicates imperfect decomposition of the feldspar by the fusion.

6. Quartz, and minerals containing very high percentages of silica, may require eight or ten parts by weight of the flux to insure a satisfactory decomposition.

7. The presence of the large quantity of sodium salts tends to increase the amount of silica which fails to become insoluble during the heating (Gilbert, *loc. cit.*). For work of the highest accuracy the remaining silica should be recovered, as outlined on page 59, note 9.

PART III.

VOLUMETRIC ANALYSIS.

GENERAL DISCUSSION.

It has already been pointed out in Part I, that the measurement of the volume of a solution required for a definite reaction, takes the place in Volumetric Analysis which is occupied by the weighing of the precipitated body in Gravimetric Analysis.

It is plain that the analytical balance is equally requisite as a starting point for both systems ; and it will be seen that the processes of volumetric analysis demand, beside an accurate balance, *standard solutions ; i. e.,* solutions of accurately known value ; *graduated instruments* in which to measure the volume of such solutions ; and finally, some means which shall furnish an accurate indication of the point at which the desired reaction is completed. Those substances which furnish such information are called *indicators.* The last-named will be treated of in connection with the different analyses.

The process whereby a standard solution is brought into reaction is called *titration,* and the point at which the reaction is exactly completed is called the *end-point.* The *indicator* should show the *end-point* of the *titration.*

The processes of Volumetric Analysis are easily classified, according to their character, into :

I. Saturation Methods ; such, for example, as those of acidimetry and alkalimetry.

II. Oxidation Processes ; as exemplified in the determination of ferrous iron, by its oxidation with potassium bichromate.

III. Precipitation Methods ; of which the titration for silver with potassium sulphocyanate solution is an illustration.

From a somewhat different standpoint the methods may be sub-divided into. (*a*) *Direct Methods*, in which the substance sought is directly determined by titration with a standard solution to an end-point ; and (*b*) *Indirect Methods*, in which the substance itself is not measured, but a quantity of reagent known to be an excess, with respect to a specific reaction, is added, and the unused excess determined by titration. Examples of the latter class will be pointed out as they occur in the procedures.

Volumetric processes are, as a rule, more rapid and frequently more accurate than gravimetric processes having the same ends in view. The number of reactions capable of adaptation as volumetric methods is, however, somewhat limited.

STANDARD SOLUTIONS.

The strength or value of a solution for a specific reaction is determined by a procedure called *Standardization*, in which the solution is brought into reaction with a definite weight of a substance of known purity. For example, a definite weight of pure sodium carbonate may be dissolved in water, and the volume of a solution of hydrochloric acid necessary to exactly neutralize the carbonate, accurately determined. From these data the strength or value of the acid is known. It is then a *standard solution.*

Standard solutions may be made of a purely empirical strength, dictated solely by convenience of manipulation, or the concentration may be chosen with reference to a system which is applicable to all solutions, and based upon chemical equivalents. Such solutions usually bear some simple relation to a *Normal Solution* of the specific reagent ; *i. e.*, they are, for example, deci-normal or centi-normal solutions.

A *Normal Solution*, as defined by Mohr (*Titrirmethode*, p. 56), contains in one liter " one equivalent of the active reagent in grams." The " equivalent in grams " may be defined as " that quantity of the active reagent which contains, replaces, unites with, or in any way, directly or indirectly, brings into reaction one gram of hydrogen."

The application of this general statement to specific cases is pointed out below.

A liter of *normal acid solution* should contain such a quantity of the reagent as will furnish 1 gram of hydrogen replaceable by a base. Accordingly, the normal solution of hydrochloric acid (HCl) should contain 36.45 grams of the gaseous compound, since that amount furnishes the requisite 1 gram of hydrogen. On the other hand, the normal solution of sulphuric acid (H_2SO_4) should contain only 49.04 grams, one half of its molecular weight.

A *normal alkali solution* should contain sufficient alkali in a liter to replace 1 gram of hydrogen in an acid. This quantity is represented by the molecular weight in grams (40.05) of sodium hydrate (NaOH), while a sodium carbonate solution (Na_2CO_3) should contain but one half the molecular weight in grams (*i.e.*, 53.05 grams) in a normal solution.

A normal solution of an *oxidizing agent* should contain one equivalent of available oxygen ; that is, sufficient oxygen to unite with 1 gram of hydrogen to form water. The amount, for example, of potassium bichromate ($K_2Cr_2O_7$), which will furnish one equivalent of available oxygen is seen from the following considerations : The bichromate yields on reduction, a salt of potassium, corresponding to the oxide K_2O, and a salt of chromium, corresponding to the oxide Cr_2O_3. The residual and available oxygen is represented by three atoms ($K_2Cr_2O_7 = K_2O + Cr_2O_3 + O_3$). Accordingly, 1 gram-molecule of the bichromate will furnish six equivalents of oxygen, or enough to oxidize 6 grams of hydrogen to water, as seen from the equation $6H_2 + 3O_2 = 6H_2O$. The definition, therefore, demands only one sixth of the molecular weight (or 49.08 grams) for a normal solution.

A liter of a normal solution of a *reducing agent* must have the same reducing power as 1 gram of hydrogen. For example, a solution of stannous chloride must contain one half of its molecular weight in grams per liter (94.97 grams), as indicated by the equations, $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$ and $H_2 + 2FeCl_3 = 2HCl + 2FeCl_2$. One gram-molecule of the stannous chloride is plainly equivalent to 2 grams of hydrogen.

Normal solutions, since they rest upon a common founda-

tion, have the advantage of uniformity. A liter of a normal solution of an acid must, of necessity, exactly neutralize a liter of normal alkali solution, and one of an oxidizing agent exactly react with a liter of a normal reducing solution, and so on. It must at the same time be remembered that the same substance may have different equivalents when used under varying conditions ; as, for example, potassium permanganate, two molecules of which yield three atoms of available oxygen (equivalent to six hydrogen atoms) in neutral solution, and five atoms of oxygen (equivalent to ten atoms of hydrogen) when used in acid solution. These facts must be considered when reference is made to a normal solution of that reagent, and the statement must specify the conditions of use.

Beside the advantage of uniformity, the use of normal solutions simplifies the calculations of the results of analyses. This is particularly true if, in connection with the normal solution, the weight of substance for analysis be chosen with reference to the molecular weight of the constituent to be determined. For illustrations of this, consult Part V, page 134.

The preparation of an *exactly* normal, half normal, or decinormal solution requires considerable time and care, as noted on page 78, and is usually carried out when a large number of analyses are to be made, or when the analyst has some other specific purpose in view. It is, however, a comparatively easy matter to prepare standard solutions which differ but slightly from the normal or half normal solutions, and these have the advantage of practical equality. That is, two approximately half normal solutions are more convenient to work with, than two which are widely different in strength. It is, however, true, that whatever advantage pertains to the use of normal solutions as regards simplicity of calculations is, to a considerable extent, lost when using these approximate solutions.

GRADUATED INSTRUMENTS.

A *burette* consists of a glass tube which is made as uniformly cylindrical as possible, and of such a bore that the

divisions which are etched upon its surface shall correspond to actual contents as far as is practicable.

The tube is contracted at one extremity, and terminates in either a glass stopcock and delivery tube (a Giessler burette), or in such a manner that a piece of rubber tubing may be firmly attached, connecting a delivery tube of glass. The rubber tubing is closed by means of a pinchcock or by a glass bead (Mohr burette).

The graduations are usually numbered in cubic centimeters, and the latter are subdivided into tenths.

A *pipette* may consist of a narrow tube, in the middle of which is blown a bulb of a capacity a little less than that which it is desired to measure by the pipette ; or it may be a miniature burette, without the stopcock or rubber tip at the lower extremity. In either case, the flow of liquid is regulated by the pressure of the finger on the top, which prevents the admission of the air.

Graduated, or measuring flasks are similar to the ordinary flat-bottomed flasks, but are provided with long, narrow necks in order that slight variations in the position of the meniscus with respect to the graduation, shall represent a minimum volume of liquid. The flasks must be of such a capacity that, when filled with the specified volume, the liquid rises well into the neck.

CALIBRATION OF INSTRUMENTS.

If accuracy of results is to be attained, the correctness of all measuring instruments must be tested. None of the apparatus offered for sale can be implicitly relied upon, unless it be those more expensive instruments which are accompanied by a certificate from the Physikalische Reichsanstalt in Berlin, or other equally authentic source.

The bore of burettes may readily vary, and as the graduations must be applied without regard to such variations of bore, local errors are the result. The same consideration applies to pipettes, while even the graduations upon flasks are often incorrect for the temperatures given. It is the custom in most laboratories to purchase the flasks ungraduated, and to graduate them for the standard in use.

The process of testing these instruments is called *Calibration.* It is usually accomplished by comparing the actual weight of water contained in the instrument with its apparent volume.

There is, unfortunately, no uniform standard of volume which has been adopted for general use in all laboratories. It has been variously proposed to consider the volume of 1000 grams of water at 4°, 15.5°, 16°, 17.5°, and even 20° C., as a liter, for practical purposes, and to consider the cubic centimeter to be one thousandth of that volume.

The true liter is the volume of 1000 grams of water at 4° C.; but this is obviously a lower temperature than that found in our laboratories, and involves the constant use of corrections, if taken as the standard. Mohr in his *Titrirmethode* adopts 17.5° C. as a practically useful temperature, and the volume of 1000 grams of water at 17.5° C. is known as the "Mohr liter." This temperature, or even 15° C., does not differ greatly from the average temperature of the laboratory, and, except when the highest accuracy is required, no corrections need be applied. It is always well, however, to note the temperature at the time of a titration, and to make proper corrections for unusual fluctuations.

When apparatus for graduation is purchased unmarked, and is calibrated in the laboratory where it is to be used, any temperature may be selected which approaches the average for that laboratory, but *all* instruments should, for convenience, be calibrated at that temperature, whether flask, burette, or pipette, since, if a 50 cc. measuring flask is to be capable of measuring exactly one tenth of the liquid contained in a 500 cc. measuring flask, both must be correct at the same temperature. The spot selected for volumetric work should be subject to a minimum of temperature change.

CALIBRATION OF BURETTES.

Each student should calibrate at least one burette as follows:

Procedure. — Clean the burette thoroughly by pouring into it a warm solution of chromic acid in concentrated

sulphuric acid. Stopper the burette and bring the acid in contact with its entire length by shaking. Pour the acid back into its receptacle, and wash out the burette thoroughly with water. Unless the water runs from the burette without leaving drops upon the sides, the process must be repeated. When clean, fill the burette with distilled water, allow it to run out through the stopcock, or rubber tip, until convinced that no air bubbles are inclosed. Fill the burette to the zero mark and draw off the liquid until the meniscus is just below the zero mark. To take the exact reading, wrap around the burette a piece of colored paper, with its straight, smooth edges held evenly together (color turned inside), and held two small divisions below the meniscus. Move the eye so that the edge of the paper at the back of the burette is just hidden by that in front, and note the position of the lowest point of the meniscus of the water. Estimate the tenths of the small divisions, corresponding to hundredths of a cubic centimeter, and record the reading in the notebook.

Weigh a 50 cc. flat-bottomed flask (of thin glass), which must be dry on the outside, to the nearest centigram. Record the weight in the notebook. Place the flask under the burette, and draw out into it about 10 cc. of water, removing any drop on the tip by touching it against the inside of the neck of the flask. Do not attempt to stop exactly at the 10 cc. mark, but do not vary more than 0.1 cc. from it. Note the time, and at the expiration of three minutes (or longer), take the reading upon the burette accurately, and record it in the notebook. Meanwhile, weigh the flask and water to centigrams and record its weight. Draw off the liquid from 10 cc. to about 20 cc. into the same flask without emptying it; weigh, and at the expiration of three minutes take the reading, and so on throughout the length of the burette. When it is completed, re-fill the burette and check the first calibration.

The differences in readings represent the apparent volume, the differences in weights, the true volumes. For example, if an apparent volume of 10.05 was found to weigh 10.03 grams, it may be assumed with sufficient accuracy that

the error in that 10 cc. amounts to 0.02 cc., or 0.002 for each cubic centimeter. The records may conveniently be made in the notebook under these headings:

Readings; Differences; Weights; Differences; Calculated Corrections.

Notes. — 1. The inner surface of the burette must be absolutely clean, if the liquid is to run off freely. Chromic acid in sulphuric acid is usually found to be the best cleansing agent, but the mixture must be warm and concentrated. This solution can be prepared by adding to concentrated commercial sulphuric acid a few crystals of potassium bichromate, and 1 cc. of water. Warm the mixture gently and pour off the solution. It is convenient to have such a solution ready at hand, as burettes frequently need cleaning. The rubber tip should be removed before the cleansing agent is added.

2. It is always necessary to insure the absence of air bubbles in the tips by running the liquid rapidly through them. These bubbles may otherwise escape during titration, and vitiate results.

3. To obtain an accurate reading, the eye must be on a level with the meniscus. · This may be attained by the use of a paper, or by using a float. The latter is useful, provided it moves freely in the burette, but care must be taken that such is the case, otherwise a float is worse than useless.

4. The eye soon becomes accustomed to estimating the tenths of the divisions. If the paper is held as directed, two divisions below the meniscus, one whole division is visible to correct the judgment. It is not well to attempt to bring the meniscus exactly to a division mark on the burette. Such readings are usually less accurate than those in which the hundredths are estimated.

5. It is obvious that it would be useless to weigh the water with an accuracy greater than that of the readings taken on the burette. The latter cannot exceed 0.01 cc. in accuracy, which corresponds to 0.01 gram.

The student should clearly understand that *all other weighings* except those for calibration, should be made accurately to 0.0001 gram.

6. A small quantity of liquid adheres to the side of even a clean burette. This slowly unites with the main body of

liquid, but requires an appreciable time. Three minutes is a sufficient interval, but not too long, and should be adopted in every instance throughout the whole volumetric practice, before final readings are recorded.

7. Should the error discovered in any interval of 10 cc. on the burette exceed 0.10 cc., it is advisable to weigh smaller portions (even 1 cc.), to locate the position of the variation of bore in the tube, rather than to distribute the correction uniformly over the corresponding 10 cc. The latter is the usual course for small corrections, and it is convenient to calculate the correction corresponding to each cubic centimeter and to record it in the form of a table or calibration card, or to plot a curve representing the values.

8. Burettes may also be calibrated by drawing off the liquid in successive portions through a 5 cc. pipette which has been accurately calibrated, as a substitute for weighing. If many burettes are to be examined this is a more rapid method.

9. Pipettes are calibrated in the same general way as burettes. They must be cleaned, and are then filled with water, and the latter is drawn off and weighed. A definite interval must be allowed for draining, and a definite practice adopted as regards the removal of the liquid which collects at the end of the tube, if the pipette be designed to deliver a specific volume when emptied. This liquid may, at the end of a definite interval, be removed either by touching the side of the vessel or by gently blowing out the last drops. Either practice must be uniformly adhered to.

CALIBRATION OF FLASKS.

Procedure. — Clean the flask and dry it carefully outside and inside. Tare it accurately, and place on the opposite balance-pan the number of grams corresponding to the volume desired; pour water into the flask until the weight of the latter counterbalances the weight on the pan. Remove the flask from the balance, stopper it, place it in a bath at the desired temperature, say, 17.5° C., and after an hour, mark on the neck with a diamond, the location of the lowest point of the meniscus.

Notes. — 1. The allowable error in counterbalancing the water and weights varies with the volume of the flask.

It should not exceed one ten-thousandth of the weight of water.

2. Other methods are used which involve the use of calibrated apparatus, from which the desired volume of water may be run into the dry flask, and the graduation marked directly upon it. For a description of one of these, the student is referred to the *Am. Chem. J.*, 16, 479.

3. Flasks may be graduated either for " contents " or for "delivery." In the former case they contain the specified volume when filled to the graduation ; in the latter case the flask will deliver the specified volume, if allowed to drain for a definite time. By placing two marks upon the flask it may be graduated for both contents and delivery.

To calibrate a flask for delivery, it should be filled with water, then emptied and allowed to drain for a definite interval (three minutes). It is then tared, the requisite weights are placed upon the balance pan, and water added to counterbalance these. It is then placed in a bath at the required temperature and, after an hour, marked.

Flasks thus calibrated will deliver a definite volume of a solution without being washed out. It is, however, a more general custom to graduate flasks for contents.

GENERAL DIRECTIONS.

It is essential to the success of analysis that uniformity of practice shall prevail throughout all volumetric work, with respect to those matters which can influence the accuracy of measurement of liquids. Whatever conditions are imposed, for example, during the calibration of a burette, pipette, or flask (notably the time allowed for draining), must also prevail *whenever* the flask or burette is used.

The student should be constantly watchful to insure parallel conditions during both standardization and analysis, with respect to the final volume of liquid in which a titration takes place. The standard of the solution is only accurate under the conditions which prevailed when it was determined.

It is plain that the standard solutions must be scrupulously protected from concentration or dilution, after their value has been established. Accordingly, great care must be taken to thoroughly rinse out all burettes, flasks, etc.,

with the solutions which they are to contain, in order to remove all traces of water, or other liquid which could act as a diluent. It is best to wash out a burette at least three times with small portions of a solution, allowing them to run out through the tip, before assuming that it is in a condition to be filled and used. It is, of course, possible to dry the measuring instruments in a hot closet, but this is tedious and unnecessary.

To the same end, all solutions should be kept stoppered, and away from direct sunlight or heat. The bottles should be shaken before use, to collect any liquid which may have distilled from the solution and condensed on the sides.

Care should be taken when selecting a spot for volumetric work, that no source of heat is sufficiently near to raise the temperature of the solutions. The temperature should always be as near 17.5° C. as is practicable.

Much time may be saved by estimating the approximate volume of a standard solution which will be required for a titration (if the data are obtainable), before beginning the operation. It is then possible to run in rapidly approximately the required amount, after which it is only necessary to determine the end-point with accuracy. In such cases, however, the knowledge of the amount probably to be required should never be allowed to influence the judgment regarding the end-point.

I. SATURATION METHODS.

ALKALIMETRY AND ACIDIMETRY.

GENERAL DISCUSSION.

STANDARD solutions of acid and alkali are required for these processes, together with such indicators as will accurately designate the point of saturation.

Standard Acid Solutions may properly be prepared from either hydrochloric, sulphuric, or oxalic acids. Hydrochloric acid has the advantage of forming soluble compounds with the alkaline earths, but its solutions cannot be boiled without loss of strength; sulphuric acid solutions may be boiled without loss, but the acid forms insoluble sulphates of three of the alkaline earths; oxalic acid can be accurately weighed for the preparation of solutions, and its solutions may be boiled without loss, but it also forms insoluble oxalates with three of the alkaline earths, and cannot be used with certain of the indicators.

Standard Alkali Solutions may be prepared from sodium or potassium hydroxide, sodium carbonate, barium hydroxide, or ammonia. Of sodium and potassium hydroxide, it may be said that they can be used with all indicators, and their solutions may be boiled, but they absorb carbon dioxide readily, and attack the glass of bottles; sodium carbonate may be weighed directly, if its purity is assured, but the presence of the carbonic acid of the carbonate is a disadvantage with many indicators; barium hydroxide solutions may be prepared which are entirely free from carbon dioxide, and such solutions immediately show by precipitation any contamination from absorption, but the hydroxide is not freely soluble in water; ammonia yields a clean solution, and does not absorb carbon dioxide as readily as the caustic alkalies, but its solutions cannot be boiled, nor can they be used with all indicators.

Half-normal ($\frac{N}{2}$) or deci-normal ($\frac{N}{10}$) solutions are employed in most analyses (except in the case of the less soluble barium hydroxide). Solutions of the latter strength are convenient, when small percentages of acid or alkali are to be determined.

INDICATORS.

An indicator, to be of service in acidimetric processes, must be a substance of basic or acid character, which, like litmus, will show by a change of color, the presence of the slightest excess of free acid or alkali. The number of organic bodies which have been proposed as indicators is large, but of these a few only have come into general use. The most important among the latter are presented in the table below, with their characteristics:

Indicator.	Reaction with acids.	Reaction with alkalies.	Use with carbonic acid, in cold solution.	Use with carbonic acid, in hot solution.	Use with ammonium salts.	Use with organic acids.
Litmus.	Red.	Blue	Unreliable.	Reliable	Reliable.	Reliable.
Methyl Orange.	Pink.	Yellow.	Reliable.	Unreliable.	Reliable.	Unreliable
Phenolphthalëin	Colorless.	Pink	Unreliable.	Reliable.	Unreliable.	Reliable.
Lacmoid.	Purple red.	Blue	Unreliable.	Reliable.	Reliable	Unreliable. (?)
Cochineal.	Purple red.	Blue.	Reliable.	Reliable	Reliable	Unreliable
Rosolic acid	Yellow	Pink	Unreliable.	Reliable.	Unreliable	Unreliable [1]
Alizarine.	Yellow.	Red.	Unreliable.	Reliable.	Reliable.	Reliable.

[1] Reliable with oxalic acid.

Litmus solution, for use as an indicator, must be specially prepared. For the details of its preparation and preservation, the student is referred to *Sutton's Volumetric Analysis*, under "Indicators." A general discussion of the subject of indicators will also be found there.

Methyl Orange (also known as Orange No. III) is not affected by carbonic acid or sulphuretted hydrogen, in cold solution, and is, therefore, the most convenient indicator for use in the presence of carbonates or sulphides, unless

organic acids are also present. The customary strength for the indicator solution is 1 gram per liter, which may be dissolved in a few cubic centimeters of alcohol, and the solution diluted.

Methyl Orange can be used in the presence of borates.

Phenolphthalëin is of special value for the titration of organic acids, provided ammonia or ammonium salts are not present. In the presence of carbonates it can only be used in hot solution. The indicator solution contains 1 gram in 100 grams of alcohol.

Lacmoid solutions should contain 1 gram in 200 cc. of alcohol. It shows a neutral reaction with the salts of some of the heavy metals, thus allowing the titration of free acid in their presence.

Cochineal solutions are prepared by treating three parts of cochineal, with two hundred parts water and fifty parts alcohol. This indicator is of special value for use with ammonia.

Of the indicators mentioned in the table, methyl orange and lacmoid are most sensitive to alkalies, and phenolphthalëin is most readily changed by acids. It is possible to obtain from the same solution an acid reaction toward phenolphthalëin and a neutral or slightly alkaline reaction toward methyl orange. It is obvious, then, that it is desirable to employ the same indicator both for standardization and analysis.

Since the indicators must require a certain quantity of acid or alkali in excess, to cause the change of color, it is also plain that only the requisite quantity (usually one or two drops of solution) should be used.

PREPARATION OF HALF—NORMAL SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE.

Procedure. — Calculate the number of cubic centimeters of aqueous hydrochloric acid (sp. gr. 1.12 or 1.2) required to furnish 36.456 grams of the gaseous compound. (For this purpose consult the table on p. 146). Measure out a volume of acid about 10 per cent. in excess of the calculated quantity into a clean 2-liter bottle, and dilute with distilled

$Na_2CO_3 : 2 HCl :: u.gm. Na_2CO_3$
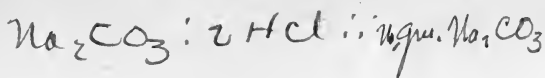
water to an approximate volume of 2000 cc.   Shake the solution thoroughly for at least a minute, to insure uniformity.

Weigh out, upon the laboratory balances, about 46 grams of sodium hydroxide.   Dissolve the hydroxide in water, and dilute to 2000 cc.   Shake this solution also for a minute.

Select two clean burettes, and fill them with the solutions, after rinsing them out *three times* with 10 cc. of the solution, which should be allowed to run out through the tip to insure the displacement of all water from that part of the burette. When the burettes are ready for use, and all air bubbles displaced from the tip, note the exact position of the liquid in each, and record the readings in the notebook.   Run out from the burette about 40 cc. of the acid into a beaker, and add two drops of a solution of methyl orange ; dilute the acid to about 100 cc., and run out alkali solution from the other burette until the pink has given place to a yellow. Wash down the sides of the beaker with a little distilled water, if the solution has spattered upon them, return the beaker to the acid burette, and again restore the pink ; continue these alternations until the point is accurately fixed at which a single small drop of either solution serves to produce a distinct change of color.   It is usually more satisfactory to select as an end-point the appearance of the faintest pink which can be recognized.   If the titration has occupied more than three minutes, the readings of the burettes may be immediately taken and recorded in the notebook.

Re-fill the burettes and repeat the titration.   Correct the burette readings as indicated by the burette calibrations, and obtain the ratio of the sodium hydroxide solution to that of hydrochloric acid by dividing the number of cubic centimeters of acid used, by the number of cubic centimeters of alkali required for neutralization.   The check results should not vary by more than 0.2 per cent. of the total ratio.

When this ratio has been fully established, weigh out, from a weighing tube, into No. 4 lipped beakers, two portions of about 1 gram each of pure calcium carbonate, noting the weights exactly (to 0.0001 gram) in the notebook. Cover the carbonate with 25 cc. of water and add two drops

of methyl orange solution; fill the burettes and note initial readings; run the acid into the beaker, with cautious stirring, until the carbonate has dissolved, avoiding loss by effervescence, wash down the sides of the beaker, and then run in alkali until the indicator becomes yellow. Finish the titration as described above. Note the readings on the burette after the proper interval, and record them in the notebook. From the data then recorded, it is possible to determine the volume of hydrochloric acid neutralized by the pure calcium carbonate, and hence the weight of gaseous hydrochloric acid in each cubic centimeter. The standardization must be repeated until these values agree within 0.2 per cent.

Compare the value just obtained with the weight of the acid which should be present in 1 cc. of $\frac{N}{2}$ HCl, and dilute the solution accordingly. (For example: a solution containing .01900 gram HCl per cubic centimeter should be diluted according to the proportion $.01900 : .01822 = x : 1000$; i. e., each 1000 cc. of that solution should be diluted to 1042.3 cc.) Measure off 2 liters accurately in a graduated flask, observing precautions mentioned on page 72, and add the requisite volume of water from a burette. From the known ratio of the two solutions, and the known value of the acid, calculate the requisite dilution for the alkali solution, and add the necessary volume of water to it also. Determine the ratio between these new solutions after shaking thoroughly, and re-standardize the acid against calcium carbonate. The values thus found should not differ from the calculated values for half-normal solutions, by more than 0.2 per cent. in either case. If a greater variation be found, the dilution and standardization must be repeated, before the solutions are ready for use.

Notes. — 1. The solutions are prepared of greater strength than that finally desired, as they are more readily diluted than strengthened. Commercial sodium hydroxide is usually impure, and always contains more or less carbonate; a further allowance is therefore made for this factor by placing the weight taken at 46 grams for the 2 liters. If the hydroxide is known to be pure, a lesser amount (say 42 grams) will suffice.

2. Too much care cannot be taken to insure perfect uniformity of solutions before standardization, and thoroughness in this respect will often avoid much waste of time. A solution once thoroughly mixed does not alter.

3. The liquid is diluted to 100 cc. during standardization to make the volume approximately equal to that which will prevail during analysis. Compare remarks on page 72.

4. The change from yellow to pink is better defined than the reverse change. The end-point should be chosen exactly at the point of change ; any darker tint is unsatisfactory, since it is impossible to carry shades of color in the memory and to duplicate them from day to day.

5. A variation of 0.2 per cent. of the total value is not excessive in a beginner's work. It must not be regarded as a fixed standard, however, or as necessarily of general application.

6. The calcium carbonate is covered with water to lessen the violence of the action of the acid. It is usually well to add a moderate excess of acid, and stir. If this fails to dissolve the carbonate, add more, and so on. The excess of acid is then neutralized by the alkali, and this excess may be calculated from the known ratio of the two solutions. This is an indirect process of standardization.

7. Anhydrous sodium carbonate may be substituted for calcium carbonate in the standardization of the acid solution, if the purity of the carbonate can be assured. It has the advantage of solubility, and is better for use with sulphuric acid since the calcium carbonate may become partially coated with insoluble calcium sulphate, and fail to be acted upon by the acid.

Instead of standardizing the acid solution as described, it is equally practicable to standardize the alkali solution against purified oxalic acid ($C_2H_2O_4.2H_2O$), potassium acid oxalate ($KHC_2O_4.H_2O$), potassium tetroxalate ($KHC_2O_4.C_2H_2O_4.2H_2O$), or potassium acid tartrate ($KHC_4H_4O_6$). The oxalic acid and the oxalates should be specially prepared to insure purity, the main difficulty lying in the preservation of the water of crystallization.

It should be noted that the acid oxalate and the acid tartrate each contain one hydrogen atom replaceable by a base, while the tetroxalate contains three such atoms, and the oxalic

acid two. Each of the two salts first named behave as mono-
basic acids, and the tetroxalate as a tribasic acid.

8.   The sulphuric acid solution may also be standardized
by precipitating the acid as barium sulphate, which is weighed
as in gravimetric analysis. Hydrochloric acid may be simi-
larly standardized by precipitation and weighing, as silver
chloride.

DETERMINATION OF THE TOTAL ALKALINE STRENGTH OF SODA ASH.

Procedure. — Weigh out, on the laboratory balances, two
portions of soda ash of about 5 grams each. Place them on
small watch-glasses and dry them at 110° C., until the weight
is constant within 0.005 grams, weighing at intervals of
thirty minutes and cooling in a desiccator. Finally weigh
accurately, and transfer the soda ash to a No. 4 lipped
beaker ; weigh the watch-glasses, and take the difference as
the weight of the sample for analysis. Dissolve the ash in
75 cc. of water, warming gently, and filter off the insoluble
residue ; wash the filter until the washings are freed from
carbonate, cool the filtrate to the temperature of the labora-
tory, and transfer it to a 250 cc. measuring flask, washing
out the beaker thoroughly. Add distilled water until the
lowest point of the meniscus is level with the graduation on
the neck of the flask, and remove any drops of water that
may be on the neck above the graduation, with a strip of
filter paper ; make the solution thoroughly uniform, by pour-
ing it out into a dry beaker and back into the flask several
times.

Measure off 50 cc. of this solution in a measuring flask,
but first pour into the smaller flask at least two small por-
tions of the soda-ash solution, and shake to displace any
water. Finally fill the flask to the mark with the solution,
and remove any drops on the neck above the graduation.
Empty it into a beaker and wash out the small flask, unless
it is graduated to *deliver* 50 cc. (Compare note 3, p. 72.)
Dilute the solution in the beaker to 100 cc., add two drops
of methyl orange solution, and titrate for the alkali with the

half-normal acid, using the half-normal alkali to complete the titration, as described under the preparation of solutions. From the corrected volumes of acid and alkali employed, and the data derived from the standardization, calculate the percentage of alkali present, assuming it all to be present as sodium carbonate.

It is advisable to measure out a second portion of 50 cc. from the main solution in each case, to confirm the original titration.

Notes. — 1. Soda ash is crude sodium carbonate. If made by the ammonia process, it may contain also sodium chloride, sulphate, and hydrate; when made by the Le Blanc process, it may contain sodium sulphide, silicate, and aluminate, and other impurities. Some of these, notably the hydrate, combine with acids and contribute to the total alkaline strength, but it is customary to calculate this strength in terms of sodium carbonate; *i. e.*, as though no other alkali were present.

2. In order to secure a sample which shall represent the average value of the ash, it is well to take at least 5 grams. As this is too large a quantity for convenient titration, an aliquot portion of the solution is measured off, representing one fifth of the entire quantity.

It is also possible to weigh out exactly 2.6525 grams of the soda ash, dissolve, filter, and titrate the entire solution, when the number of cubic centimeters of half-normal acid used will indicate directly the alkaline strength in terms of sodium carbonate. The student should verify this statement by calculation.

3. It is customary to dry the soda ash at 110° C. before analysis. Greater uniformity of results is then attainable.

Complete expulsion of the moisture would require a temperature just below the fusion point of the carbonate.

4. The residue insoluble in water must be completely washed to remove soluble alkali, and the filtrate must be cooled to a temperature approximating 17.5° C. before dilution to a definite volume, in a measuring flask which is correct at that temperature.

A 50 cc. pipette may be equally well employed to measure out the aliquot portion, in place of the 50 cc. flask.

5. The determination of the caustic alkali in the soda ash may be accomplished by precipitating the carbonate with barium chloride, removing it by rapid filtration, and titrating for the alkali in the filtrate. The carbonated alkali is then calculated as the difference between the caustic alkali and the total alkali.

DETERMINATION OF THE ACID STRENGTH OF OXALIC ACID.

Procedure. — Weigh out two portions of the acid of about 1 gram each. Dissolve these in 50 cc. of warm water, filter, if the solution is not clear, and wash the filter completely with hot water, until freed from oxalic acid. Add to the filtrate two drops of phenolphthalëin solution, and run in alkali from the burette until the solution is pink; add acid from the other burette until the pink is just destroyed, and then add 0.5 cc. (*not more*) in excess. Heat the solution to boiling for three minutes. If the pink returns during the boiling, discharge it with acid and again add 0.5 cc. in excess and repeat the boiling. If the color does not then reappear, add alkali until it does, and a *drop or two* of acid in excess and boil again for one minute. If no color reappears during this time, complete the titration in the hot solution, ending with the change from colorless to pink. From the corrected volume of alkali required to react with the oxalic acid, calculate the weight of the latter present, in terms of the crystallized acid $(C_2H_2O_4.2H_2O)$, and from this, the percentage purity of the sample.

Notes. — 1. It has already been pointed out that it is desirable to employ the same indicator throughout standardization and analysis, a statement which is applicable in this instance. The student is advised, if practicable within the time devoted to the subject, to re-standardize acid and alkali using phenolphthalëin as the indicator, and concluding each titration by boiling the solution as described above, or, what is perhaps better, to standardize the alkali solution against one of the substances named in note 7, page 79, using phenolphthalëin.

The differences resulting from the change of indicator are small, and the student may neglect them in this instance, performing the titration as outlined above to gain some practice with phenolphthalëin ; but it should be remembered that if the highest accuracy is desired, a re-standardization throughout is essential.

2.   All commercial caustic soda contains some carbonate, and as phenolphthalëin is acted upon by carbon dioxide, the solution must be boiled to expel the gas.   Phenolphthalëin does not show an alkaline reaction with acid carbonates; hence solutions containing carbonates and this indicator become colorless when *half* the carbonate has been acted upon by acid.   Upon boiling, the bicarbonate loses carbon dioxide, forming normal carbonate, and the pink returns.   This must be again discharged, and the solution boiled, and so on.

A similar procedure is necessary with all the indicators mentioned, except methyl orange ; the latter does not, however, give reliable results with organic acids, as its own acid is stronger than many of them.

It is possible to remove the carbonate from the caustic alkali by the cautious addition of barium hydroxide before standardization ; the barium carbonate is removed by filtration.

3.   Hydrochloric acid is volatilized from aqueous solutions, except such as are very dilute.   If the directions in the procedure are strictly followed, no loss of acid need be feared, but the amount added in excess must not exceed 0.5 cc.

4.   The end-point should be the faintest visible shade of color, as the same difficulty would exist here as with methyl orange, if an attempt were made to match shades of pink.

II. OXIDATION PROCESSES.

Under this section may properly be included, beside oxidation processes, the rather limited number of methods in which standard solutions of reducing agents only are employed, since a corresponding oxidation of the reducing agent must always be a part of the reaction. In general it may be stated that *oxidizable* substances are determined by direct titration, while *oxidizing* substances are usually determined by indirect methods.

Many quantitative determinations are made possible by the application of these volumetric methods involving oxidation or reduction, which are not practicable by gravimetric procedures. A notable example is that of the determination of iron in the presence of aluminum. The mixture of hydroxides thrown down by ammonia may be ignited, weighed, and the iron subsequently determined volumetrically, by solution of the precipitate, reduction of the iron, and oxidation by potassium permanganate or bichromate. The aluminum is then determined by difference.

The important oxidizing agents employed for volumetric solutions are potassium bichromate, potassium permanganate, potassium ferricyanide, iodine, ferric chloride, and sodium hypochlorite.

The important reducing agents which are used in the form of standard solutions are ferrous sulphate (or ferrous ammonium sulphate), oxalic acid, sodium thiosulphate, stannous chloride, and arsenious acid. Other reducing agents, as sulphurous acid, sulphuretted hydrogen, and zinc (nascent hydrogen) take part in the processes, but not as standard solutions.

The most important combinations among the foregoing are the following : Potassium bichromate and ferrous salts ; potassium permanganate and ferrous salts ; potassium permanganate and oxalic acid ; iodine and sodium thiosulphate; hypochlorites and arsenious acid.

BICHROMATE PROCESS FOR THE DETERMINATION OF IRON.

GENERAL DISCUSSION.

Ferrous salts may be promptly and completely oxidized to ferric salts, even in cold solution, by the addition of potassium bichromate, provided sufficient free acid is present to combine with, and hold in solution, the ferric iron resulting from the oxidation.

The free acid may be either hydrochloric or sulphuric, but the former is usually preferred, since it is by far the best solvent for iron and its compounds. The reaction in the presence of hydrochloric acid is as follows; $6 \, FeCl_2 + K_2Cr_2O_7 + 14 \, HCl = 6 \, FeCl_3 + 2 \, CrCl_3 + 2 \, KCl + 7 \, H_2O$.

The weight of potassium bichromate necessary for a normal solution was shown on page 65 to be 49.08 grams. It is possible to prepare a standard solution of the bichromate by directly weighing the requisite quantity, and dissolving it in a definite quantity of water. The commercial salt, though rarely sufficiently pure for this purpose as it often contains potassium sulphate, may be purified by re-crystallization from hot water, but must then be dried, and finally heated to fusion to expel the last traces of moisture. The fusion temperature must not be exceeded, as the bichromate will lose oxygen if more strongly heated.

It is, perhaps, a more satisfactory mode of procedure to make up a solution of the commercial salt and determine its strength by comparison with iron, either in the form of iron wire of known purity, or ferrous ammonium sulphate, $FeSO_4. (NH_4)_2SO_4. 6 \, H_2O$. A standard wire is now offered in the market which answers the purpose well, and its iron contents may be determined for each lot by a number of gravimetric determinations. It may be best preserved in jars containing calcium chloride but this must not be allowed to come in contact with the wire. It should, however, even then be carefully examined for rust, before use.

If ferrous ammonium sulphate is used as the standard, clear crystals only must be selected, and it is perhaps even better to determine by gravimetric methods, once for all, the iron contents of a sample which has been ground and mixed.

It is well to have on hand a solution of this salt for use in connection with the bichromate. Such a solution is more stable if about 5 cc. of concentrated sulphuric acid per liter, are added.

It is plain that all of the iron in the solution must be in the ferrous condition before titration. The available agents for the reduction of any ferric iron are stannous chloride, sulphurous acid, sulphuretted hydrogen, and zinc; of these stannous chloride acts most readily, the completion of the reaction is most easily noted, and the excess of the reagent is most readily removed. The latter object is accomplished by oxidation by means of mercuric chloride added in excess, as the mercury salts have no effect upon ferrous iron or the bichromate. The reactions involved are $2 \ FeCl_3 + SnCl_2 = 2 \ FeCl_2 + SnCl_4$; and $SnCl_2 + 2 \ HgCl_2 = SnCl_4 + 2 \ HgCl$. The mercurous chloride is precipitated.

It is essential that the solution should be cold and that the stannous chloride should not be present in great excess, lest a secondary reaction take place, resulting in the reduction of the mercurous chloride to metallic mercury : $SnCl_2 + 2 \ HgCl = SnCl_4 + 2 \ Hg$. The occurrence of this secondary reaction is indicated by the darkening of the precipitate, and since potassium bichromate oxidizes this mercury slowly, solutions in which it has been precipitated are worthless as iron determinations.

No indicator has been found which may be used within the solution, on account of the deep green of chromium salts ; the use of potassium ferricyanide outside the solution is therefore necessary to detect the presence of ferrous iron. A drop of the iron solution and one of the indicator solution are brought together on a white surface — best a porcelain tile — and examined for a blue precipitate of the ferrous ferricyanide. It is plain that the potassium ferricyanide must contain no ferrocyanide, for which it should be carefully tested. The latter, if present, may

be oxidized by the addition of a little bromine to the solution, after which the ferricyanide must be recrystallized.

The indicator solution must be very dilute to diminish the interference of its own color ; a crystal the size of the head of a pin in 25 cc. of water is an ample quantity. This solution must be freshly prepared each day, as the dilute solution is not stable.

No metals may be present in the titrated solution which, like iron, are reduced by stannous chloride and oxidized by potassium bichromate : notably, copper, antimony, and platinum. For this reason a platinum crucible must never be allowed to remain in an iron solution, as ferric chloride exerts a slight solvent action upon the platinum.

The bichromate solution may be placed in burettes with rubber tips without danger of deterioration of the solution.

STANDARDIZATION OF A POTASSIUM BICHROMATE SOLUTION.

Procedure. — Pulverize about 5 grams of potassium bichromate, dissolve it in water, and dilute to approximately 1000 cc.

Pulverize about 40 grams of ferrous ammonium sulphate, dissolve it in water, dilute to about 1000 cc., and add 5 cc. of concentrated sulphuric acid. It is not necessary to select clear crystals of the sulphate.

Shake the solutions until they are uniform, and place them in burettes, with the precautions mentioned on page 77.

Prepare a solution of potassium ferricyanide of the strength recommended above, and place single drops of this solution on the surface of a porcelain tile.

Run out from a burette into a beaker about 40 cc. of the ferrous solution, add 15 cc. of hydrochloric acid (sp. gr. 1.12), dilute it to 150 cc., and run in the bichromate solution from another burette. Since both the solutions are approximately deci-normal, 35 cc. of the bichromate solution may be added without testing. Test at that point, by removing a very small drop of the iron solution on the end of a stirring rod, and mixing it with a drop of indicator on the tile.

If a blue precipitate appears at once, 0.5 cc. of the bichro-
mate solution may be run out before testing again. The
stirring rod which has touched the indicator should be dipped
in distilled water, before returning it to the iron solution.
As soon as the blue appears to be less intense, add the
bichromate solution in small portions, finally a single drop
at a time, until the point is reached at which no blue color
appears after the lapse of thirty seconds from the time of
mixing solution and indicator on the tile, the time being
accurately noted. At the close of the titration a large drop
of the iron solution should be taken for the test. To deter-
mine the end-point beyond any question, as soon as the thirty
seconds have elapsed remove another drop of the solution
of the same size as that last taken, and mix it with the
indicator, placing it beside the last previous test. If this
last previous test shows a blue tint in comparison with the
fresh mixture, the end-point has not been reached; if no
difference can be noted the reaction is complete. Should
the end-point be overstepped, more ferrous ammonium sul-
phate solution may be added.

From the corrected volumes of the solutions used, cal-
culate the value of the ferrous solution in terms of the ox-
idizing solution.

Weigh out two portions of iron wire, of about 0.24–0.26
grams each, examining the wire carefully for rust. It
should be handled and wiped with wash-leather, not touched
by the fingers, should be weighed on a watch-glass, and be
so bent as not to interfere with the movement of the
balance.

Dissolve the wire in a covered beaker in 30 cc. of hydro-
chloric acid (sp. gr. 1.12), warming gently; wash off the
cover and sides of the beaker, and add stannous chloride
solution to the hot liquid, from a dropper, until the solution
is colorless, but avoid more than a drop or two in excess.
Dilute with 150 cc. of water, and cool *completely*. When
cold, add rapidly about 30 cc. of mercuric chloride solu-
tion (50 grams per liter). Allow the solutions to stand
three minutes and then titrate without delay, as just
described. Calculate the volume of the bichromate solution

which would be required if the solution were deci-normal, and add about this quantity. The ferrous ammonium sulphate solution may be used if the end-point is passed, and much time saved.

From the corrected volumes of the bichromate solution required to oxidize the iron actually present in the wire, calculate the value of each cubic centimeter in terms of iron (Fe), and also the amount of iron in each cubic centimeter of the ferrous ammonium sulphate solution. Record these values in the notebook.

Repeat the standardization until the results for the value of each cubic centimeter in terms of iron are concordant within 0.00001 gram.

Notes. — 1. Note carefully the statements in the "General Discussion" bearing upon the steps in the standardization.

2. The hydrochloric acid is added to the ferrous solution to insure the presence of sufficient free acid for the titration.

3. The time interval for the indicator tests must be carefully noted. Some time must elapse before the completion of the reaction when the ferrous iron is nearly all oxidized, but if left too long, the combined effect of light and dust causes a reduction and a deposition of a blue precipitate, as in the process of "blue-printing." Thirty seconds is a necessary and also a sufficient interval.

4. The accuracy of the work may be much impaired by the removal of unnecessarily large quantities of solution for the tests. At the beginning of the titration, while much ferrous iron is still present, the end of the stirring rod need only be moist with the solution, but at the close of the titration drops of considerable size may properly be taken for the final tests. The stirring rod should be washed to prevent transfer of indicator to the main solution.

If the end-point is determined as prescribed, it can be as accurately fixed as that of other methods, and if a ferrous solution is at hand, the titration need consume hardly more time than that of the permanganate process, to be described later on.

5. The solution should be allowed to stand about three minutes after the addition of mercuric chloride to permit the

complete deposition of mercurous chloride. It should then be titrated without delay to avoid re-oxidation of the iron by the oxygen of the air.

6. The potassium bichromate solution may be diluted to form an exactly deci-normal solution if desired, according to the principles stated on page 78.

DETERMINATION OF IRON IN LIMONITE.

Procedure. — Grind the mineral to a fine powder, weigh out two portions of about 0.5 gram into No. 7 porcelain crucibles, heat these crucibles to dull redness for ten minutes, allow them to cool, and place them, with their contents, in beakers containing 30 cc. of hydrochloric acid (sp. gr. 1.12). Heat at a temperature just below boiling until the undissolved residue is white, or until solvent action has ceased; if a dark residue remains, collect it on a filter, wash free from hydrochloric acid, and ignite the filter in a platinum crucible. Mix the ash with a small quantity of sodium carbonate and heat to fusion; cool, and dissolve the fused mass in boiling water in the crucible. Unite solution and precipitate (if any) with the acid extraction, washing out the crucible; heat the solution to boiling, add stannous chloride solution until it is colorless, avoiding a large excess, cool, and when *cold*, add 40 cc. of mercuric chloride solution, and proceed with the titration as already described on page 87.

Calculate the percentage of iron (Fe) in the limonite.

Notes. — 1. Limonite is a native, hydrated oxide of iron. It frequently occurs in or near peat beds, and contains more or less organic matter, which, if brought into solution, would be acted upon by the potassium bichromate. This organic matter is destroyed by roasting. Since a high temperature tends to lessen the solubility of ferric oxide, the heat should not be raised above low redness.

2. A white residue, or one known to be free from iron, may be neglected, and need not be filtered off.

3. The quantity of stannous chloride required for the reduction of the iron in the limonite will be much larger than that added to the solution of iron wire, in which the iron was mainly ferrous. It should, however, be added from a dropper.

4. The platinum crucible, if used for the carbonate fusion, must not be put into the iron solution. A platinum crucible may also be used for the roasting, if preferred, with the same precaution with respect to the iron solution.

5. It is sometimes advantageous to dissolve a large portion — say, 5 grams — and to take one tenth of it for titration. The sample will then probably represent more closely the average value of the ore.

DETERMINATION OF CHROMIUM IN CHROME IRON ORE.

Procedure. — Fuse 10 grams of borax to a glass in a large platinum crucible. Grind the chrome iron ore to the finest powder, and weigh into the crucible about 0.5 gram. Heat over a Bunsen burner, and stir with a stout platinum wire until a clear glass is formed; transfer the crucible to the blast lamp, add 2 grams of sodium carbonate, and heat to quiet fusion, using the highest temperature attainable.

Mix 1.5 gram of sodium carbonate and 1.5 grams of potassium nitrate, and divide the mixture into six portions. Project these portions into the crucible at suitable intervals, watching carefully after each addition to prevent loss of material, particularly with the last portions. Stir the liquid mass occasionally, and continue the heating until no more gas is evolved.

Cool the crucible, remove the fused mass as described on page 32, and place both in a casserole; boil with water until the fused mass is disintegrated, remove the crucible, wash it carefully, and add sulphuric acid to the solution in slight excess. Run in ferrous ammonium sulphate solution from a burette until the ferrous iron is in excess, and titrate for that excess with the potassium bichromate solution.

From the corrected volumes of the two standard solutions, calculate the amount of iron oxidized by the chromium from the chrome iron ore, and subsequently the weight of chromium in solution and the percentage in the ore.

> *Notes.* — 1. Chrome iron ore is essentially a ferrous chromite, or combination of FeO and Cr_2O_3. The borax glass dissolves these oxides, and the nitrate oxidizes them to ferric oxide (Fe_2O_3) and chromic anhydride (CrO_3), the latter combining with the alkali to form sodium chromate. The excess of nitrate is decomposed, leaving the alkali as oxide, which combines with some of the non-volatile acids present. After fusion, the chromium is in the same state of oxidation as in the bichromate solution, and reacts in the same way with the ferrous salt.

Each atom of chromium in the ore is capable of oxidizing three atoms of iron: $2 Cr_2O_3 + 3 O_2 = 4 CrO_3$; $6 FeSO_4 + Na_2Cr_2O_7 + 7 H_2SO_4 = 3 Fe_2(SO_4)_3 + Na_2SO_4 + Cr_2(SO_4)_3 + 7 H_2O$.

2. After the oxidation of the chromium is approximately complete, the effervescence increases with each addition of the oxidizing mixture, and greater care is required to avoid loss. The determination requires constant attention while the crucible is over the blast lamp.

The use of a graphite jacket to surround the crucible makes easier the maintenance of a high temperature, but is not indispensable. Occasional stirring prevents the accumulation of undecomposed material at the bottom of the crucible.
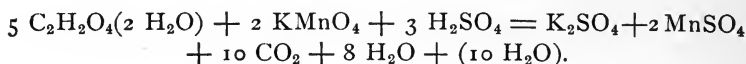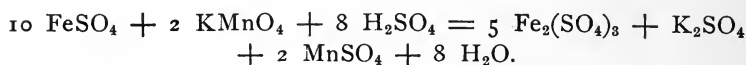
3. If a standard solution of a ferrous salt is not at hand, a weight of iron wire, somewhat in excess of that required if the substance were pure chromic oxide (Cr_2O_3), may be weighed out, dissolved in acid, reduced with stannous chloride, and treated as in the standardization of the bichromate solution. The excess of iron is then determined by means of the latter.

PERMANGANATE PROCESS FOR THE DETERMINA-
TION OF IRON.

GENERAL DISCUSSION.

Potassium permanganate oxidizes ferrous salts, in cold, acid solution, promptly and completely to the ferric condition, while in hot, acid solution it also enters into a definite reaction with oxalic acid, by which the latter is oxidized to carbon dioxide and water.

The reactions involved are these:

$$10 \ FeSO_4 + 2 \ KMnO_4 + 8 \ H_2SO_4 = 5 \ Fe_2(SO_4)_3 + K_2SO_4 \\ + 2 \ MnSO_4 + 8 \ H_2O.$$

$$5 \ C_2H_2O_4(2 \ H_2O) + 2 \ KMnO_4 + 3 \ H_2SO_4 = K_2SO_4 + 2 \ MnSO_4 \\ + 10 \ CO_2 + 8 \ H_2O + (10 \ H_2O).$$

These are the fundamental reactions upon which its extensive use depends, but beside iron and oxalic acid, the permanganate enters into reaction with tin, copper, mercury, and manganese (the latter only in neutral solution), by which these metals are changed from the lower to the higher state of oxidation, and it also reacts with sulphurous acid, sulphuretted hydrogen, nitrous acid, ferrocyanides, and most soluble organic bodies. It should be noted that it is only with oxalic acid, among organic compounds, that there is a definite reaction suitable for quantitative purposes.

From the definition of a normal oxidizing solution (page 65) the normal solution of potassium permanganate for use in the presence of acid must contain 31.62 grams of the reagent. This is seen from the following considerations: Two molecules of the permanganate yield, as shown in the equations above, one molecule of potassium salt corresponding to the oxide K_2O, and two molecules of manganous salt corresponding to the oxide MnO, leaving five available oxygen atoms ($2 \ KMnO_4 = K_2O . 2 \ MnO. O_5$). The five oxygen atoms furnished by the two gram-molecules of the permanganate (316.2 grams) are equivalent to 10 grams of hydrogen. Accordingly, the normal solution must contain one

tenth of two gram-molecules, or one fifth of one gram-molecule ; *i. e.*, 31.62 grams.

In neutral solution the permanganate is decomposed as indicated by the equation $2\ KMnO_4 = K_2O.\ 2\ MnO_2.\ O_3$. The normal solution for such purposes should contain one sixth of two gram-molecules ; *i. e.*, 52.7 grams.

Potassium permanganate is acted upon by hydrochloric acid ; the action is rapid in hot or concentrated solutions but slow in cold, dilute solutions. The use of the permanganate in the presence of hydrochloric acid, or its salts, may therefore be attended by the possibility of error, and it is usually preferable to replace the hydrochloric acid of iron solutions by sulphuric acid, before titration. This may be done by evaporation with an excess of the latter until the heavy, white fumes of sulphuric anhydride appear.

The greater solubility of iron compounds in hydrochloric acid makes it desirable to titrate, if possible, directly in such solutions, and experiments made with this end in view have shown that in cold, dilute hydrochloric acid solutions, to which considerable quantities of manganous sulphate or chloride, and an excess of phosphoric acid have been added, it is possible, with practice, to obtain satisfactory results ; but the end-point is less permanent than in sulphuric acid solutions. Such a process is described in the *J. Am. Chem. Soc.*, **17**, 405. The reaction between hydrochloric acid and the permanganate is :

$$2\ KMnO_4 + 16\ HCl = 2\ KCl + 2\ MnCl_2 + 5Cl_2 + 8\ H_2O.$$
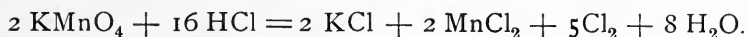
Potassium permanganate has an intense coloring power, and, since the solution resulting from the oxidation of the iron and the reduction of the permanganate is colorless, the latter becomes its own indicator. The slightest excess is indicated with great accuracy by the color of the solution, which renders the titration one of the most satisfactory known.

The commercial salt is rarely sufficiently pure to admit of direct weighing to form a standard solution, but it may be purified by re-crystallization. The more common practice is

to standardize the solution, which may be accomplished by comparison with iron wire, ferrous ammonium sulphate, oxalic acid, potassium tetroxalate, or potassium acid oxalate. Other substances have been proposed, but the foregoing are those in common use.

The remarks on page 85 referring to the use of iron wire and ferrous ammonium sulphate apply with equal force here. The pure oxalic acid, or the oxalates, must be freshly prepared, and with great care; they are likely to lose water of crystallization on standing. It must also be borne in mind that the reaction with the oxalates takes place only in hot solution.

The reducing agents available for the necessary reduction of the iron before titration, are zinc, sulphurous acid, or sulphuretted hydrogen; stannous chloride is excluded unless the titration is to be made in the presence of hydrochloric acid. Since the excess of both the gaseous reducing agents can only be expelled by boiling, with consequent uncertainty regarding the re-oxidation of the iron, zinc is the more satisfactory agent; but for prompt and complete reduction it is essential that the solution should be brought into intimate contact with the zinc. This is brought about by the use of a modified Jones reductor, as shown in the figure, page 97.*

To prevent needless consumption of the zinc, it is first amalgamated by dissolving 5 grams of mercury in 25 cc. of concentrated nitric acid, diluted with an equal bulk of water, and pouring into this solution (diluted to 250 cc. in a 1000 cc. flask), 500 grams of granulated zinc, 20–30 mesh. The whole is shaken thoroughly for two minutes, the solution poured off, and the zinc washed thoroughly. It may then be preserved in bottles.

The tube *A* has an inside diameter of 18 mm., and is 300 mm. long; the small tube has an inside diameter 6 mm., and extends 100 mm. below the stopcock. At the base of the tube *A* is coiled a piece of stout platinum wire; on this is placed a plug of glass wool about 8 mm. thick, and upon

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* The details of the reductor and preparation of the zinc are taken from *Blair's Chemical Analysis of Iron*, page 95 *et seq.*

this a thin layer of asbestos, such as is used for Gooch filters, 1 mm. thick. The tube is then filled with the amalgamated zinc to within 50 mm. of the top, and on the zinc is placed a plug of glass wool. The 60 mm. funnel B is fitted into the tube with a rubber stopper, and the reductor is connected with a suction bottle, F. The bottle D is a safety bottle to prevent contamination of the solution by water from the pump.

The iron solution during its passage through the reductor comes into intimate contact with the zinc, and is reduced by the nascent hydrogen evolved. The column of zinc should never be less than five inches in length. *Great care* must be used to prevent the access of air to the reductor after it has been washed out ready for use. If air enters, hydrogen peroxide forms, which reacts with the permanganate, and the results are worthless.

It is also possible to reduce the iron by treatment with zinc, in a flask from which air is excluded, the zinc being completely dissolved. This method is, however, less convenient and more tedious than the reductor.

Potassium permanganate solutions are not usually stable for long periods, and change more rapidly when first prepared than after standing some days. This is probably
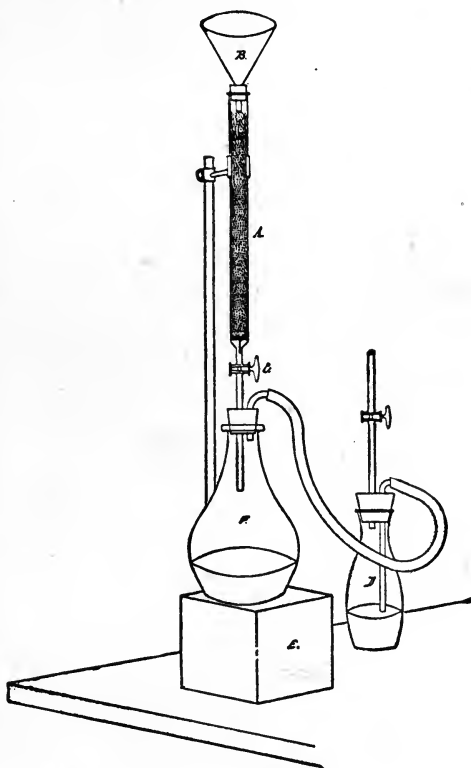
caused by interaction with the organic matter contained in all distilled water, except that distilled from an alkaline permanganate solution. The solutions should, however, be protected from the light as far as possible, since sunlight induces decomposition, with a deposition of manganese dioxide, and it has been recently shown* that the decomposition proceeds with considerable rapidity, with the evolution of oxygen, after the dioxide has begun to form. As commercial samples of the permanganate are likely to be contaminated by the dioxide, it is advisable to filter solutions through asbestos before standardization. Such solutions are relatively stable.

The permanganate solution cannot be placed in burettes with rubber tips, as a reduction takes place upon contact with the rubber. The solution has so deep a color that the lower line of the meniscus cannot be detected ; readings must therefore be made from the upper edge.

STANDARDIZATION OF A POTASSIUM PERMANGANATE SOLUTION.

Procedure. — Dissolve about 3.25 grams of potassium permanganate crystals in 200 cc. of water, in a beaker, warming to hasten solution. Filter through a layer of asbestos, cool, dilute to about 1000 cc., and mix thoroughly. Fill a glass-stoppered burette with this solution, observing usual precautions, and fill a second burette with the ferrous ammonium sulphate solution prepared for use with the potassium bichromate. Run out into a beaker about 40 cc. of the iron solution, add 10 cc. of dilute sulphuric acid (1 : 5), and run in the permanganate solution to a slight permanent pink. Repeat, until the ratio of the two solutions is fixed.

Weigh out into beakers two portions of iron wire of about 0.25 gram each. Dissolve these in dilute sulphuric acid (5 cc. of concentrated acid and 100 cc. of water), warming to promote solution. Meanwhile prepare the reductor for use

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* Morse, Hopkins, and Walker, *Am. Chem. J.*, **18**, 401.

as follows: Connect the suction bottle with the vacuum pump, fill the reductor while the stopcock is closed (or nearly so) with warm dilute sulphuric acid (5 cc. of acid in 100 cc. water), and then open the stopcock so that the acid runs through slowly. Continue to pour in acid until 200 cc. have passed through, then close the cock *while a small quantity of liquid is still left in the funnel.* Remove the filtrate, and again pass through 100 cc. of the warm, dilute acid. Test this with the permanganate solution. A single drop should color it permanently; if it does not, repeat the washing. Be sure that no air enters the reductor.

Pour the iron solution while hot (but not boiling) through the reductor at a rate not exceeding 50 cc. per minute. Wash out the beaker with dilute sulphuric acid, and follow the iron solution, without interruption, with 175 cc. of the warm acid, and finally with 75 cc. of distilled water, leaving the funnel partially filled. Remove the filter bottle, and cool the solution under the water tap. Add 10 cc. of dilute sulphuric acid, and titrate to a faint pink with the permanganate solution directly in the filter bottle. Should the end-point be overstepped, the ferrous ammonium sulphate solution may be added. From the volume of the solution required to oxidize the iron in the wire, calculate the value of each cubic centimeter in terms of metallic iron (Fe). The results should be concordant within 0.00001 gram.

Notes. — 1. A careful study of the "General Discussion" should be made in connection with the steps of this and the following procedure.

2. The funnel of the reductor must never be allowed to empty, and if it is left partially filled, the reductor is ready for subsequent use without the previous washing. A preliminary test is always a safeguard against error, however.

If more than a small drop of permanganate solution is required to color 100 cc. of the dilute acid after the reductor is well washed, an allowance must be made for the iron in the zinc.

The rate of filtration of the iron solution should not exceed that prescribed, but the rate may be increased somewhat when the wash-water is added. It is well to allow the

iron solution to run nearly, but not entirely, out of the funnel before the wash-water is added. If it is necessary to inter-rupt the process, the complete emptying of the funnel can always be avoided by closing the stopcock.

It must be borne in mind that only the *nascent* hydrogen is efficient as a reducing agent. That which is visible is molecular hydrogen and without influence upon the ferric iron.

3. The dilute sulphuric acid for washing must be warmed ready for use before the reduction of the iron begins.

4. The end-point is more permanent in cold than hot solutions, possibly because of a slight action of the perman-ganate upon the manganous sulphate formed during the titra-tion. If the solution turns brown, it is an evidence of insuf-ficient acid, and more should be immediately added. The results are likely to be less accurate in this case, however, as a consequence of secondary reactions between the fer-rous iron and the manganese dioxide thrown down.

5. The potassium permanganate may, of course, be diluted and brought to an exactly $\frac{N}{10}$ solution from the data here obtained. The percentage of iron in the iron wire, as estab-lished by gravimetric methods, must be taken into account in the calculation.

DETERMINATION OF IRON IN LIMONITE.

Procedure. — Weigh out two portions of the powdered limonite, roast, and bring them into solution as described on page 90, but dissolve finally in casseroles. Add cau-tiously to the solution 5 cc. of concentrated sulphuric acid, and evaporate on the steam bath until the solution is nearly colorless. Cover the casseroles and heat over the flame of the lamp until the heavy white fumes of sulphuric anhy-dride are freely evolved. Cool the casseroles, add 100 cc. of water, and boil until the ferric sulphate is dissolved; pour the warm solution through the reductor, proceed as described under standardization, and titrate with the per-manganate solution in the filter flask, using the ferrous ammonium sulphate solution, if need be. From the volume of permanganate solution used, calculate the equivalent quantity of iron (Fe), and the percentage in the limonite.

Notes. — 1. The preliminary roasting is probably necessary, even though the sulphuric acid subsequently chars the carbonaceous matter. Certain nitrogenous bodies are not rendered insoluble in the acid, and would be oxidized by the permanganate.

2. The hydrochloric acid, both free and combined, is displaced by the less volatile sulphuric acid at its boiling point. The ferric sulphate separates at this point, since there is no water to hold it in solution, and care is required to prevent bumping.

3. The ferric sulphate usually has a silky appearance, and is easily distinguished from the flocculent silica which remains undissolved. A small quantity of glass wool may be placed in the neck of the funnel to prevent the passage of this silica into the reductor.

DETERMINATION OF THE OXIDIZING POWER OF PYROLUSITE.

Pyrolusite, when pure, consists of manganese dioxide. Its value, as an oxidizing agent and for the production of chlorine, depends upon the percentage of MnO_2 in the sample. This percentage is determined by an indirect method, in which the manganese dioxide is reduced and dissolved by an excess of ferrous sulphate or oxalic acid, and the unused excess determined by titration with permanganate.

Procedure. — Grind the mineral in an agate mortar until no grit whatever can be detected when the powder is placed between the teeth. Dry the ground sample on a watch-glass at 110° C. for an hour, transfer it to a stoppered weighing tube, and weigh out two portions of about 0.5 gram into No. 3 beakers. Calculate the weight of oxalic acid ($C_2H_2O_4$. 2 H_2O) required to react with the weights of pyrolusite taken for analysis, assuming it to be pure manganese dioxide : $MnO_2 + C_2H_2O_4(2 H_2O) + H_2SO_4 = MnSO_4 + 2 CO_2 + 2H_2O + (2 H_2O)$. Weigh out about 0.2 gram in excess of this quantity of *pure* oxalic acid into the corresponding beakers, weighing the acid accurately, and recording the weight in the notebook. Cover the beakers, and pour into each 25 cc. of water and 50 cc. of dilute sulphuric acid (1 : 5) ; warm the liquid gently, until the evolution of carbon dioxide ceases. If a residue remains which is sufficiently colored to obscure the end-reaction of the permanganate, it must be removed by filtration.

Finally, heat the solution to a temperature just below boiling, and, while hot, titrate for the excess of the oxalic acid with potassium permanganate solution. From the corrected volume of the solution required, calculate the amount of oxalic acid undecomposed by the pyrolusite; subtract this from the total quantity of acid used, and calculate the weight of manganese dioxide which would react with the balance of the acid, and from this the percentage in the sample. Consult Part V, page 134.

Notes. — 1. The success of the analysis is largely dependent upon the fineness of the powdered mineral. If properly ground, solution should be complete in fifteen minutes or less.

2. The ground pyrolusite is somewhat hygroscopic. It should be dried at a low temperature (110°), as a higher heat tends to expel water of constitution from hydrated oxides which may also be present.

3. A moderate excess of oxalic acid above that required to react with the pyrolusite is necessary to promote solution; otherwise the residual quantity of oxalic acid would be so small that the last particles of the mineral would scarcely dissolve. It is also desirable that a sufficient excess of the acid should be present to react with a considerable volume of the permanganate solution during the titration.

4. Care should be taken that the sides of the beaker are not overheated, as oxalic acid would be decomposed by heat alone, if crystallization should occur on the sides of the vessel. Strong sulphuric acid also decomposes the oxalic acid. The dilute acid should, therefore, be prepared outside the beaker.

5. Ferrous ammonium sulphate or iron wire may be substituted for the oxalic acid. The reaction is then the following: $2 FeSO_4 + MnO_2 + 2 H_2SO_4 = Fe_2 (SO_4)_3 + MnSO_4 + 2 H_2O$. The excess of ferrous iron may also be determined by means of potassium bichromate, if desired.

Great care is required to prevent the oxidation of the iron by the air, if ferrous salts are employed.

6. Other volumetric processes may be employed for this determination, one of which is outlined in the following reactions: $MnO_2 + 4 HCl = MnCl_2 + Cl_2 + 2 H_2O$; $Cl_2 + 2 KI = I_2 + 2 KCl$; $I_2 + 2 Na_2S_2O_3 = Na_2S_4O_6 + 2 NaI$. The chlorine generated by the pyrolusite is passed into a solution of potassium iodide. The liberated iodine is then determined by titration with sodium thiosulphate, as described on page 107. This is a direct process, although it involves three steps.

It is also possible to absorb and weigh the liberated carbon dioxide evolved during the reaction with the oxalic acid, and from this weight to find the percentage of manganese dioxide in the sample. This is a gravimetric process.

IODIMETRY.

GENERAL DISCUSSION.

The titration of iodine against sodium thiosulphate, with starch as an indicator, may perhaps be regarded as the most accurate of volumetric processes. It may be used both in acid and in neutral solutions to measure free iodine, and the latter may, in turn, serve as a measure of any substance capable of liberating iodine from potassium iodide under suitable conditions for titration. For example : the quantity of potassium bromate in a commercial sample of that salt may be determined through the following reactions : $KBrO_3 + 6 KI + 3 H_2SO_4 = 3 K_2SO_4 + KBr + 3 I_2 + 3 H_2O$, and $I_2 + 2 Na_2S_2O_3 = Na_2S_4O_6 + 2 NaI$.

Another illustration is afforded by the process outlined in note 6, page 103.

Iodine is an oxidizing agent, and, as such, must conform to the same conditions as other similar bodies, with respect to its normal solutions. From the equation $SO_2 + I_2 + H_2O = SO_3 + 2 HI$, it is plain that 126.85 grams of iodine suffice to liberate the oxygen necessary to oxidize 1 gram of hydrogen, and that, accordingly, that weight of iodine is requisite for a normal solution. Deci- and centinormal iodine solutions are commonly used.

Iodine acts as an oxidizing agent either through the decomposition of water, in the presence of an oxidizable body, as illustrated by the reaction $As_2O_3 + 2 I_2 + 2 H_2O = As_2O_5 + 4 HI$, or by increasing the proportion of the negative constituent of a compound through the direct withdrawal of the positive component, as typified by the equations : $2 Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2 NaI$, and $H_2S + I_2 = 2 HI + S$.

The tendency of the iodine to combine with hydrogen is not sufficient to cause it to decompose water, unless some body be present which will readily combine with the oxygen thus set free.

A complete equipment for iodimetric work requires solu-

tions of iodine, sodium thiosulphate, potassium iodide, and starch.

Commercial iodine requires re-sublimation before it can be regarded as sufficiently pure to be weighed for a standard solution. It should be sublimed between watch-glasses, after the addition of potassium iodide to unite with any chlorine present in combination with the iodine, and should be subsequently dried over sulphuric acid. It may then be dissolved in a stoppered flask, in a solution of potassium iodide (about 18 grams of the iodide to 12 of the iodine), and diluted to a definite volume.

Its solutions are decomposed by sunlight, with the formation of hydriodic acid, and a high temperature tends to volatilize the iodine. They are not stable for long periods, and require frequent standardization, against arsenious acid, anhydrous sodium thiosulphate, or standard solutions of the latter.

Iodine solutions act upon rubber; hence only burettes with glass stopcocks should be used.

Sodium thiosulphate ($Na_2S_2O_3 \cdot 5 H_2O$) is rarely wholly pure as sold commercially, but may be purified by crystallization, if need be. The carbon dioxide absorbed from the air by distilled water decomposes the salt, with the separation of sulphur, and if standard solutions are to be prepared directly, boiled water, which has been cooled out of contact with the air, must be used.

Solutions of the thiosulphate must be protected from light and heat, both of which promote decomposition. They may be standardized against pure iodine, or — with the intervention of potassium iodide — against potassium bromate, potassium iodate, or potassium bichromate. The reactions on page 104 indicate the principle involved.

It should be noted that chlorine and bromine oxidize the thiosulphate to sulphate, while the iodine leads only to the formation of sodium tetrathionate, $Na_2S_4O_6$.

Commercial potassium iodide generally contains a small quantity of iodate, which, in acid solution, liberates iodine, as indicated by a yellow coloration. The reaction is: $KIO_3 + 5 KI + 3 H_2SO_4 = 3 K_2SO_4 + 3 I_2 + 3 H_2O$. The

iodate is not necessarily uniformly distributed through the iodide, and, in order that an accurate blank test for iodate may be made, which shall apply to each analysis, it is necessary to bring a considerable quantity of the iodide into solution, and to take a measured volume of this solution for each analysis. The strength is adapted to the work in hand.

The starch solution, for use as an indicator, must be freshly prepared. A soluble starch is now obtainable which serves well, and a solution of 0.5 gram of this starch in 25 cc. of boiling water is sufficient. It is ready for use when cold, and from 1 cc. to 2 cc. suffices.

If soluble starch is not at hand, potato starch may be used. Mix about 1 gram with 5 cc. of cold water to a smooth paste, pour 150 cc. of *boiling* water over it, warm for a moment on the hot plate, and put it aside to settle. Decant the supernatant liquid through a filter and use the clear filtrate. 5 cc. of this solution are needed for a titration.

The solution of potato starch is less stable than the soluble starch. The solid particles of the starch, if not removed, become so colored by the iodine that they are not readily decolorized by the thiosulphate.

The iodo-starch blue is discharged by caustic alkalies, or normal carbonates of the fixed alkalies, but not by the bicarbonates.

STANDARDIZATION OF IODINE AND SODIUM THIOSULPHATE SOLUTIONS.

Procedure. — Weigh out, on the laboratory balances, 13 grams of commercial iodine. Place it in a mortar with 18 grams of potassium iodide and triturate with small portions of water until all is dissolved. Dilute the solution to 1000 cc.*

Weigh out 25 grams of sodium thiosulphate, dissolve it in water, and dilute to 1000 cc.

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* It will be found more economical to have a considerable quantity of the solution prepared by a laboratory attendant, and to have all unused solutions returned to the common stock.

Place these solutions in burettes (the iodine in a glass-stopped burette), observing the usual precautions to prevent dilution. Run out 40 cc. of the thiosulphate solution into a beaker, dilute with 150 cc. of water, add 1 cc. to 2 cc. of the soluble starch solution, and titrate with the iodine to the appearance of the blue of the iodo-starch. Repeat, until the ratio of the two solutions is established.

(*Method A.*)

Weigh out, into No. 4 beakers, two portions of 0.175–0.200 gram each, of pure arsenious acid. Dissolve in 10 cc. of sodium hydroxide solution, with stirring. Dilute the solutions to 150 cc. and add hydrochloric acid until the solution contains a few drops in excess, and finally add a concentrated solution of 5 grams of sodium bicarbonate ($HNaCO_3$). Cover the beakers to avoid loss. Add the starch solution, and titrate with the iodine to the appearance of the blue of the iodo-starch, taking care not to pass the end-point.

From the corrected volume of the iodine solution used to oxidize the arsenious acid, calculate the quantity of iodine in each cubic centimeter, and its relation to the normal. From the ratio between the solutions, calculate similar values for the thiosulphate solution.

(*Method B.*)

Weigh out into No. 4 beakers two portions of about 0.150–0.175 gram of potassium bromate, or potassium iodate. Dissolve these in 50 cc. of water and add a sufficient volume of potassium iodide solution to furnish 3 grams of the salt. Add to the mixture 10 cc. of dilute sulphuric acid (1 : 5), allow the solution to stand for three minutes, and dilute to 150 cc.; run in thiosulphate solution from a burette until the color of the iodine is nearly destroyed, then add 1 cc. to 2 cc. of starch solution, titrate to the disappearance of the iodo-starch blue, and finally add iodine solution until the color is just restored. Make a blank test for the amount of thiosulphate solution re-

quired to react with the iodine liberated by the iodate in the potassium iodide solution, and deduct this from the total volume used in the titration.. From the data obtained, calculate the weight of thiosulphate in each cubic centimeter of the solution, and its relation to a normal solution, and, subsequently, similar values for the iodine solution.

Notes. — 1. The two methods of standardization seem to yield equally satisfactory results, and the student is advised to try both. The arsenious acid and the potassium salts both require careful examination to establish their purity. The former usually requires re-sublimation, and the two latter re-crystallization.

2. The color of the iodo-starch is somewhat less satisfactory in concentrated solutions of alkali salts, notably the iodides. The dilution prescribed obviates this difficulty.

3. Arsenious acid dissolves more readily in caustic alkali than in the bicarbonates, but the presence of caustic alkali during the titration is not admissible. It is, therefore, destroyed by the addition of acid, and the solution is then made alkaline with the bicarbonate. Normal carbonates of the fixed alkalies cannot be used.

The reaction during titration is the following:

$$Na_3AsO_3 + I_2 + 2\ HNaCO_3 = Na_3AsO_4 + 2\ NaI + 2\ CO_2 + H_2O.$$
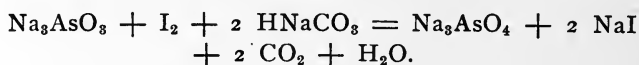
As the reaction between sodium thiosulphate and iodine is not always free from secondary reactions in the presence of even the weakly alkaline bicarbonate, it is best to avoid the addition of any considerable excess of iodine. Should the end-point be passed by a few drops, the thiosulphate may be used to correct it.

4. The potassium iodide should be measured from a stock solution for the reasons stated on page 105. It is then possible to make an accurate blank test for the iodate.

DETERMINATION OF ANTIMONY IN STIBNITE.

The sample for analysis should be pure, leaving, at most, only a siliceous residue.

Procedure. — Weigh out two portions of about 0.35–0.40 gram of the mineral (which should be well ground), into two small dry beakers (No. 2). Pour over the stibnite 5 cc. of hydrochloric acid (sp. gr. 1.20) and warm gently, but keep well below the boiling point. When the residue is white, add to each 1 gram of solid tartaric acid. Dilute the solution very cautiously by adding water in portions of 5 cc., stopping as soon as the solution turns red. It is possible that no coloration will appear, in which case cautiously continue the dilution to 125 cc. If a red precipitate or coloration does appear, warm the solution until it is colorless and again dilute cautiously. Continue this to a total volume of 125 cc., and boil for a minute.

Meanwhile, dissolve 6 grams of sodium bicarbonate in 200 cc. of water, in a No. 6 beaker; pour the cold acid solution of the antimony into this, avoiding loss by effervescence. Make sure that the solution contains an excess of the bicarbonate, and then add 1 cc. to 2 cc. of starch solution and titrate with iodine solution to the appearance of the blue, avoiding an excess.

From the corrected volume of the iodine solution required to oxidize the antimony, calculate the weight of the latter in the solution and the percentage in the stibnite.

Notes. — 1. The success of this determination is largely dependent upon close adherence to the directions as given, particularly with respect to the amounts of reagents and the dilution.

2. Antimony chloride is volatile with the steam from its concentrated solutions; hence these solutions must not be boiled until they have been diluted.

3. The separation of antimony oxy-chloride from solutions of the chloride, on dilution with water, is prevented by the addition of the tartaric acid.

4. Stibnite is native antimony sulphide, and upon solution in hydrochloric acid sulphuretted hydrogen is liberated, a part of which is absorbed by the acid, unless the heating is long continued. Upon dilution, a point is reached at which the sulphide of antimony, being no longer held in solution by the acid, separates. If the dilution is immediately

stopped and the solution warmed, this sulphide is again brought into solution and at the same time some of the sulphuretted hydrogen is expelled. This procedure must be continued until the sulphuretted hydrogen is all removed, since it reacts with iodine. ($H_2S + I_2 = 2\ HI + S.$)

If no precipitation of the sulphide occurs, it is an indication that it was all expelled immediately after solution.

5. If, for any reason, a white precipitate of the oxychloride separates during dilution (which should not occur if the directions are followed), it is best to discard the determination and to start anew.

6. The reaction between the iodine and the antimony is parallel with that between iodine and arsenious acid.

CHLORIMETRY.

GENERAL DISCUSSION.

Under chlorimetry are included those processes by which not only free chlorine, but also bromine, hypochlorous and hypobromous acids are estimated. The reagent employed is arsenious acid, in bicarbonate solution. In this weakly alkaline solution the reaction between chlorine and the arsenious acid is parallel with that of iodine.

A solution of arsenious acid which has been prepared from the pure acid may be used without standardization, and is stable for long periods, but the commercial acid requires re-sublimation to remove arsenic sulphide, which may be present in small quantity. To prepare the solution, dissolve about 5 grams of the powdered acid, accurately weighed, in 10 cc. of a concentrated sodium hydroxide solution, dilute the solution to 300 cc., and make it faintly acid with hydrochloric acid. Add 30 grams of sodium bicarbonate, and dilute the solution to 1000 cc. in a measuring flask. If desired, the value of this solution may be checked by titration against the standardized iodine solution.

The indicator required is made by dipping strips of filter paper in a starch solution, to which 1 gram of potassium iodide has been added. These strips are allowed to drain and spread upon a watch-glass. When touched by a drop of the solution, the paper turns blue until an excess of the arsenious acid has been added. The paper must be moist when used.

DETERMINATION OF THE AVAILABLE CHLORINE IN BLEACHING POWDER.

Procedure. — Weigh out from a stoppered test-tube into a porcelain mortar, about 3.5 grams of bleaching powder. Keep the mortar away from the door of the balance case, to avoid injury to the balance. Triturate the powder in the mortar with successive portions of water, until it is well ground and transferred to a 500 cc. measuring flask. Fill

the flask to the graduation and shake thoroughly. Measure off 25 cc. of this semi-solution in a measuring flask, or pipette, observing the precautions named on page 80, and the further precaution that the liquid removed shall contain its proportion of suspended matter.

Empty the flask into a beaker and wash it out. Run in the arsenious acid solution from a burette, until no further reaction takes place with the starch-iodide paper when touched by a drop of the solution of bleaching powder. From the volume of solution required to react with the bleaching powder, calculate the percentage of chlorine in the latter, assuming the titration reaction to be that between chlorine and arsenious acid. Note that one twentieth of the total weight of bleaching powder enters into the reaction.

Notes. — 1. Bleaching powder may be regarded as containing both calcium chloride and hypochlorite. Its efficiency, when treated with acids, depends upon the quantity of the latter constituent, since the hydrochlorous acid yields as bleaching agents both oxygen and chlorine. It is customary, however, to express the value of the bleaching agent in terms of available chlorine, as though only that were a factor in its efficiency. The chlorine present as chloride is, of course, not available for bleaching purposes.

2. Bleaching powder readily loses chlorine on exposure to the air, as a result of the absorption of carbon dioxide. The sample must be carefully protected, but even then it is rarely possible to obtain closely agreeing results from separate samples. For technical purposes, it is usually sufficient to examine one sample. The student should check his results by titrating two portions from the 500 cc.

3. The powder must be triturated until it is fine, otherwise the lumps will inclose calcium hypochlorite, which will fail to react with the arsenious acid. The clear supernatant liquid gives percentages which are below, and the sediment percentages which are above the average. The liquid measured off should, therefore, carry with it its proper proportion of the sediment.

III. PRECIPITATION METHODS.

SULPHOCYANATE PROCESS FOR THE DETER-
MINATION OF SILVER.

GENERAL DISCUSSION.

The addition of a solution of potassium or ammonium sulphocyanate to one of silver in nitric acid, causes a deposition of silver sulphocyanate, as a white curdy precipitate. If ferric nitrate is also present, the slightest excess of the sulphocyanate, over that required to combine with the silver, is indicated by the deep red which is characteristic of the sulphocyanate test for iron,

The reactions involved are: $AgNO_3 + KSCN = AgSCN + KNO_3$, and $3 KSCN + Fe(NO_3)_3 = Fe(SCN)_3 + 3 KNO_3$.

The normal solution of the sulphocyanate should contain a sufficient quantity of the salt to combine with 1 gram of hydrogen to form sulphocyanic acid ; *i. e.*, a gram-molecule, or 97.23 grams KSCN. The sulphocyanate cannot be accurately weighed; its solutions must, therefore, be standardized against silver nitrate, either in the form of a standard solution, or by weighing out small portions. An $\frac{N}{20}$ solution of the sulphocyanate is the strength to be used for titrations.

The reaction with silver may be carried out in nitric acid solution, and in the presence of copper, if the latter does not exceed 70 per cent. Above that percentage it is necessary to add silver, in known quantity, to the solution.

The liquid must be cold at the time of titration and entirely free from nitrous compounds.

A saturated solution of ferric alum, to which a moderate quantity of nitric acid has been added, serves as an indicator. The volume used is 5 cc. and should be the same for each titration.

STANDARDIZATION OF A POTASSIUM SULPHOCYANATE SOLUTION.

Procedure. — Crush a few crystals of silver nitrate in a mortar, transfer them to a watch-glass, and dry for an hour at 110° C. Protect the nitrate from dust or organic matter. Weigh out two portions of about 0.5 gram each. Dissolve these in 50 cc. of water and add 10 cc. of nitric acid (sp. gr. 1.2), which has been recently boiled, and 5 cc. of the indicator solution. Run in the sulphocyanate solution from a burette, until a faint red tinge can be detected in the solution after vigorous stirring. From the corrected volume used, calculate the value of the solution in terms of metallic silver, and its relation to a normal solution. Repeat, until the results are concordant.

Notes. — 1. The crystals of silver nitrate sometimes inclose water, which is expelled on drying. If the nitrate has come into contact with organic bodies, it suffers a reduction and blackens during the heating.

2. It is plain that a standard solution of silver nitrate (made by weighing out the crystals) is convenient or necessary, if many titrations of this nature are to be made. In the absence of such a solution, the liability of passing the endpoint is lessened by setting aside a small fraction of the silver solution, which can be added at the close of the titration to counteract any accidental excess of sulphocyanate.

DETERMINATION OF SILVER IN COIN.

Procedure. — Weigh out two portions of the coin, of about 0.5 gram each. Dissolve them in 15 cc. of nitric acid (sp. gr. 1.2), and boil until all the nitrous compounds are expelled; cool the liquid, dilute to 50 cc., add 5 cc. of the indicator solution, and titrate with the sulphocyanate to the appearance of the faint red coloration.

From the corrected volume of the sulphocyanate solution required, calculate the weight of silver present, and the percentage in the coin.

Note. — These solutions, containing the silver precipitate, as well as those from the standardization, should be placed in the receptacle for "silver residues."

PART IV.

THE THEORIES OF SOLUTIONS AND SOME OF THEIR APPLICATIONS TO ANALYTICAL CHEMISTRY.*

BEFORE the development of what may be termed the modern theories concerning the conditions under which substances exist in solution, the exact nature of those chemical reactions which are the chief dependence of the analyst was so little understood, that all attempts to increase the accuracy of quantitative separations were made on empirical grounds, and were dictated solely by the results of experimentation. With the acceptance and expansion of these theories has come the possibility of approaching such problems from a theoretical standpoint, and of directing experimentation along logical lines, the advantages of which have been most marked. In the following pages these modern conceptions will be briefly stated; but the student is urged to broaden his acquaintance with the literature bearing upon them as time and interest permit.

It will be remembered that experiment has shown that all gases, of whatever chemical character, show uniformity of behavior under changing pressure, obeying the law of Boyle that the volume of a specific quantity of a gas varies inversely as its pressure, and that they all, in obedience to the law of Gay-Lussac, expand equally for equal increments of temperature. This uniformity of deportment is consistent only with the assumption that equal volumes of all gases, under like conditions of temperature and pressure, contain the

* In the preparation of this chapter the author has made free use of *Ostwald's Scientific Foundations of Analytical Chemistry*, of which he wishes to make full acknowledgment. The student is referred to that work for a more extended treatment of the topics than is given in these few pages. The brief outline here given is intended to serve chiefly as a foundation for later study, and as an incentive to further thought and reading.

same number of molecules, or separate particles, and that
these phenomena are dependent only upon the number of
these particles, and not upon their chemical nature.   A
study of gases bears out this hypothesis, and also the
assumption that, in general terms, these particles move
through the space occupied by the gas independently of
each other.

Recent investigations have apparently furnished grounds
for the further hypothesis that substances in solution (par-
ticularly in dilute solution) may be compared with the same
substances in the gaseous state, and that, if a pressure (the
existence of which in a solution may be experimentally
proven, and which is called *osmotic* pressure) be substituted
for gas pressure, the same laws apply to the behavior of
these bodies in dilute solution as in the gaseous state.   As
before, the assumption seems justified that these physical
phenomena may be ascribed to the numbers of unit parti-
cles present, and not to their chemical nature, and that the
molecules of solvent may be regarded as without influence
upon the independence of the movement of the molecules
of the dissolved substance, since they act upon all alike.
But it has also been shown by experiment that when the
body in solution is capable of conducting electricity, being
itself decomposed at the same time (that is, when the sub-
stance is an electrolyte), there is a larger number of unit
particles in the solution than is in accordance with the above
hypothesis, and also a larger number than is found in a
solution of an equivalent quantity of an indifferent body,
or non-electrolyte.   Such abnormal conditions are noted
chiefly in aqueous solutions of electrolytes.   A study of
the apparently abnormal behavior of this class of bodies led
Arrhenius to propose his now generally accepted Theory of
Electrolytic Dissociation, which assumes that salts, acids,
and bases — in short, electrolytes — in aqueous solution do
not exist solely in the usual molecular condition, but are
dissociated to a greater or less degree into electrically
charged atoms, or groups of atoms, called ions.   The posi-
tive ions (cathions) are the metals, basic radicals, or hydro-

gen, on the one hand, and the negative ions (anions) are the acid radicals, or hydroxyl, on the other; as, for example, K and Cl in potassium chloride; $2 (NH_4)$ and SO_4 in ammonium sulphate; H and Cl in hydrochloric acid; Na and OH in sodium hydroxide.

These ions are not to be regarded as identical with the elementary substances, sodium, chlorine, etc., in the ordinary condition in which they are more familiar, since each ion bears a charge of positive or negative electricity, which alters its chemical and physical properties to a marked degree. In any solution the amount of one kind of electric charge must be exactly equal to that of the other sort; for, the moment that this equilibrium is disturbed by the discharge of any portion of either sort of electricity — as, for example, when an electric current is passed through the solution,— the ions immediately pass to the one or the other pole, and appear there with their usual properties. Thus, when a solution of copper sulphate is submitted to the action of an electric current, the copper ions pass with the positive electricity to the negative pole, and there lose their electric charge, and are deposited as metallic copper. In a similar way the SO_4 ions pass to the positive pole, where, when the charge is removed, they react with a molecule of water to form sulphuric acid, with the evolution of oxygen.

The ions may be regarded as differing from the corresponding molecular bodies in the amount of energy with which they are endowed, and even ions of identically the same chemical composition, but of differing valency, may exhibit widely different properties. For example, the ion MnO_4 in the permanganates (as $KMnO_4$) yields a purple-red solution, and behaves chemically in a way far different from the ion MnO_4 in the manganates (as K_2MnO_4), which is green in solution.

The degree of dissociation for specific dilutions varies with the substance; it increases with increasing dilution, and is theoretically only complete at infinite dilution. The degree of dissociation can be determined by a study of the electrical conductivity of the solutions, and by other

methods, which, however, do not need to be discussed in this connection. The electrolytes may be separated into three general classes with respect to the degree of their dissociation : 1. Those substances which at moderate dilutions are very largely dissociated (say, 60 to 90 per cent.) — for example, almost all salts ; strong acids, like hydrochloric, sulphuric, and nitric acids ; and strong bases, as the hydroxides of the alkalies and alkaline earths. 2. Substances of comparatively slight dissociation (say, 1 to 20 per cent.) at ordinary dilution, as phosphoric, sulphurous, acetic, and most of the organic acids, and ammonia. 3. Those substances of which a very small percentage only (less than 1 per cent.) is dissociated at ordinary concentrations — as, for example, weak acids, such as carbonic, boracic or hydrocyanic acids, and hydrogen sulphide ; and weak bases, as the hydroxides of di- and trivalent metals. The "strength" of an acid or base corresponds, then, in general terms, with its degree of dissociation or "ionization," in solution.

The halogen compounds of cadmium and mercury form exceptions to the general statement regarding the degree of dissociation of salts. These compounds are relatively little dissociated at ordinary dilutions. No explanation of this abnormal behavior has been offered.

It has also been shown experimentally that the chemical properties exhibited by a solution of any body are those of its ions, and that when an element or radical is not present in an ionized state those properties which are considered typical, and upon which reliance is placed for its identification or its separation, are lacking. For example, potassium chloride is dissociated into K and Cl ions in aqueous solution, and the chlorine is easily detected by precipitation with silver nitrate ; but neither chloroform ($CHCl_3$), nor potassium chlorate ($KClO_3$) in aqueous solution show the typical reaction for chlorine, since the former is a non-electrolyte, and the ions of the latter are K and ClO_3. The analytical tests are, then, the tests for ions, and analytical chemistry is the chemistry of ions ; and a ready explanation is thus offered for the fact that the test for any element or radical

(for example, copper or sulphuric acid) is the same, no matter what the other element or radical may be with which it was associated in the molecule, provided that the molecule is dissociated in solution. This is made apparent to the eye by the fact that the ions often produce characteristic colors in solutions. Thus, all cupric salts (except those in which the copper is associated with some other colored ion) color dilute solutions blue. All chromates in dilute solutions are yellow and dichromates red, since the ion CrO_4 (as in K_2CrO_4) is yellow, while the ion Cr_2O_7 is red in solution. A study of solutions with respect to changes in color under conditions of varying ionization has led to useful results. The applications in the case of indicators used in volumetric analysis will be made later (page 129).

The task of the quantitative analyst most frequently involves the separation from solution of the substance to be determined, in some form, or in some combination which permits of *quantitative accuracy*, and his chief aim is to establish conditions which will permit of such a separation. Although it is true that the solubility of many bodies in many solvents is less than can be measured by known means, yet, from theoretical considerations, it may be asserted that no body is absolutely insoluble in any given solvent; and it is further true that many substances employed for quantitative separations are, even under carefully maintained conditions, appreciably soluble. It is in showing how this solubility may be reduced to a minimum that the development of and deductions from the theory of Arrhenius have been of great value.

Take, for example, an instance of quantitative precipitation, as that of the sulphate ions from a solution of ammonium sulphate by means of barium chloride (page 32). To explain this fully it is necessary to consider briefly the question of chemical equilibrium, as it exists at the moment when a quantity of the precipitant has been added which is theoretically sufficient to complete the desired reaction. The

compounds in solution, being salts, are largely ionized into the ions 2 (NH_4) and SO_4, and Ba and 2Cl. Suppose that the addition of the barium chloride were to cease at the instant when a number of Ba ions has been added exactly corresponding to the number of (SO_4) ions present. The compound $BaSO_4$, being relatively insoluble, separates from the solution for the most part, but not absolutely, since a small quantity is still soluble, forming a saturated solution of that sulphate. The state of equilibrium which is immediately produced is called heterogeneous, because bodies in different states of aggregation are involved. First, there is equilibrium between the precipitated barium sulphate and that which remains in solution. For such cases of heterogeneous equilibrium there must be, at the contact surfaces, a definite ratio of concentration for the existing conditions of temperature. This may be expressed by the equation $c' = kc$, in which c and c' are respectively the concentrations of the precipitated sulphate and the non-ionized sulphate in the solution, and k is a constant, depending upon the substance and the temperature. Since, in this instance, the one body (the precipitated sulphate) is a solid, its concentration (c) does not change ; hence the expression $c' = kc$ simply states that, for a given temperature, the concentration (c') of the non-ionized sulphate in solution is a constant quantity.*

Turning to the dissolved sulphate and remembering that as a salt it is largely dissociated, it is found that a second condition of equilibrium exists between the undissociated and the ionized portions. The law of mass action, the truth of which has been established by experiment, states that the chemical action of a body is proportional to its concentration. In the application of this law to electro-

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* The concentration of the solid sulphate is regarded as unchanging, since no more of the barium sulphate remains in solution when the precipitate weighs 5 grams than when it weighs 1 gram, or even less. The concentration c' does not refer to the total barium sulphate in solution, but only to the non-ionized portion ; for, as is seen from the next paragraphs, the undissolved sulphate does not stand in definite relations to the concentration of the indvidual ions, but to their product.

lytes the ions must be regarded as independent bodies, as well as the undissociated molecules of the compound. The application of the law to the case of equilibrium between the ions Ba and SO_4, and the non-ionized $BaSO_4$, makes it possible to express the existing relations by the equation $ab = k'c$,* in which a represents the concentration of the Ba ions, b that of the SO_4 ions, and c that of the undissociated $BaSO_4$. k' is again a constant belonging to the barium sulphate. The product of the concentrations of the ions (ab) is called by Ostwald the "solubility-product," and a solution is saturated with a given substance (as the barium sulphate in this instance) when the product of the concentrations of the ions is sufficient to yield this solubility-product. When it is exceeded the solution becomes supersaturated, and precipitation should follow; as long as the value corresponding to saturation is not reached, more of the substance will pass into solution. This simple principle underlies the entire question of precipitation from solutions.

A sufficient number, then, of the SO_4 ions which it is desired to remove from the solution have remained dissolved to form, with the Ba ions, the solubility-product of barium sulphate. If, now, an additional quantity of barium chloride is added, the concentration of the Ba ions is at once increased — *i. e.*, the value of a is increased; but since, for constant temperature, c must remain constant, the product ab must also be constant, and the concentration b must be correspondingly reduced. This can only happen as a result of the separation from the solution of some of the SO_4 ions in the form of barium sulphate, and a further addition of barium chloride would cause further deposition of the SO_4 ions, and so on, but precipitation could never be absolutely complete as long as any of the solvent remained; it can, however, be reduced to a quantity which is negligible.

The deduction to be made from the foregoing is the simple rule, that precipitation may be made more complete

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* In those instances in which the substance is dissociated into ions of varying valency the equation takes the form $a^n b^m = kc$, where n and m represent the number of the respective ions.

by the addition to the solution of some substance containing an ion in common with the precipitate. This is usually effected by adding a moderate excess of the precipitant, this excess to be determined by considerations of expediency. In the case cited, an undue excess of barium chloride is to be avoided, on account of the tendency of the sulphate to drag out of solution other bodies which may be present with it. (See page 33, note 1.)

It is clear that the more soluble the precipitate, the greater must be the increase of the concentration of the ion added, to reduce the solubility of the precipitated ion to the desired minimum. The precipitate of magnesium ammonium phosphate is a relatively soluble body; the proportion of precipitant required to reduce its solubility to a negligible quantity is, therefore, relatively large; but, as before, the amount must be limited to a reasonable excess.

It should also be noted that the value of k is large, and of c small, for precipitates in solution if they are salts, since these would be practically completely ionized at such small concentrations.

The same principle is made use of when a wash water is employed containing a substance which has an ion in common with the precipitate treated, as in the case of lead sulphate and dilute sulphuric acid (page 50). A further application of the principle is made in the preparation of pure salt, as remarked on page 22, note 1, and in the use of an ammoniacal wash water for magnesium ammonium phosphate (page 37). In the latter instance, the alcohol is added simply as a medium in which the precipitate is but little soluble.

It must be noted that some bodies tend to form supersaturated solutions, from which they separate only slowly and on long standing, as is the case with ammonium phospho-molybdate. In such solutions the solubility-product, corresponding to equilibrium, is, it is true, exceeded, but the solutions are unstable, and the addition or formation of a minute particle of the dissolved substance leads to a separation of the solid until conditions consistent with saturation

are reached. The same result is brought about by vigorous shaking or stirring, as in the case the magnesium ammonium phosphate (page 37).

It is not always easy to determine by inspection into what ions a compound will separate in solution, and the problem is often complicated by the intervention of secondary reactions, by which complex radicals, which at first act as entities, subsequently dissociate into simpler ions. This must be borne in mind in considering questions involving equilibrium.

It must also be noted that many precipitates are redissolved to a greater or less extent by an excess of a precipitant (in apparent contradiction to the principles just laid down), as a result of the formation of double salts with complex molecules or ions. This is referred to again on page 127.

Again, it is found that in certain cases in which the ions differ in valency, as in dibasic acids, the ionization may take place as follows: $H_2\overline{A} = \overset{+}{H} + \overline{HA}$, and subsequently $H\overline{A} = \overset{+}{H} + \overline{A}$. As the first hydrogen ion behaves as that of a stronger acid than the second, and so on, it appears that these atoms differ somewhat in strength. This is illustrated by the behavior of phosphoric acid H_3PO_4. The first H ion is of medium strength, the second that of a weak acid, while the third can hardly be replaced.

Complex ions are formed from such compounds as H_2PtCl_6, which separates into 2 H and $PtCl_6$, and $K_4Fe(CN)_6$, which yields 4 K and $Fe(CN)_6$.

When two or more electrolytes are brought together in solution, the resulting phenomena are governed by principles similar to those laid down for the special case of precipitation already cited.

Two salts, such as potassium chloride and sodium nitrate, which furnish no ions capable of forming an insoluble body,

exert no action the one upon the other. Both are largely ionized, and the only bodies which could result from an interaction, namely, sodium chloride and potassium nitrate, are also equally dissociated into ions identical with those of the original compounds.

If, however, the ions are capable either of uniting to form a substance with a smaller solubility-product on the one hand, or, on the other hand, a compound which, under the existing conditions, is less ionized than those from which it is formed, an interaction takes place in that direction, and the ions disappear, as such, to form the non-dissociated substance. If the solubility-product is sufficiently small, a precipitate falls, as in the case of the barium sulphate, while the reaction between sodium hydrate and hydrochloric acid may be taken as an example of lessened ionization. The ions in the latter case are Na and OH, and H and Cl. As water is among the least dissociated bodies, the H and OH ions disappear to form non-ionized water. (It is estimated that it would require 1,000,000 liters of water to furnish 1 gram of hydrogen ions.)

The same statement is true when nitric acid and potassium hydroxide, or hydrochloric acid and barium hydroxide react, from which it is evident that the net effect of the neutralization of the acid by the alkali, in each case, is the formation of non-ionized water; and the fact that the heat of neutralization is the same in each of these cases, for equivalent quantities of acid and alkali, is explained.

Similarly, if hydrochloric acid is added to a solution of sodium acetate (or the reverse), an interaction takes place, whereby the H ions of the hydrochloric acid unite with the $C_2H_3O_2$ ions from the sodium salt, to form acetic acid, which, as a weak acid, is relatively little dissociated. The hydrogen ions of the mineral acid are thus largely withdrawn from the solution in the form of the non-ionized acetic acid. But, since acetic acid is far more largely dissociated than water, this reaction will never approach as near completion as the one previously mentioned. With a salt of a still weaker acid the reaction would be more complete, while the addition of

hydrochloric acid to a cold solution of a nitrate (the two acids being ionized to about the same degree) produces no effect with respect to the ions.

Similar principles may be applied to the behavior of strong and weak bases.

The "strength" of an acid, as has been stated, depends upon the degree to which it is ionized — that is, upon the concentration of its hydrogen ions; and the "strength" of a base upon the concentration of its hydroxyl ions. Any cause which alters these concentrations lessens or increases the efficiency of the compound. If to a solution of a weak acid, a salt of the same acid is added, the strength of the latter is lessened. For example, the addition of sodium acetate to acetic acid makes of it a weaker acid. If the solution of the acid alone is regarded, the state of equilibrium is expressed by the equation $ab = kc$, where a is the concentration of the H ions, b that of the $C_2H_3O_2$ ions, c that of the undissociated acid, and k is a constant applying to acetic acid. If, now, sodium acetate is added to the solution, of which the ions are Na and $C_2H_3O_2$, the concentration b of the latter is at once increased.

Since acetic acid is a substance which is but little dissociated, much the larger part of the acid is present in the non-ionized condition, and the concentration (c) represents approximately that of the entire quantity of acid present (a and b are relatively small in comparison with c). It is clear, then, that while c may be *slightly* increased, it cannot grow to any large extent; and since b is disproportionately increased by the addition of a large number of $C_2H_3O_2$ ions from the acetate, a must diminish, and accordingly some of the H ions unite with the $C_2H_3O_2$ ions to form a small additional quantity of undissociated acid. That is, the concentration of the hydrogen ions, which was small at the start, diminishes, and the acid power is weakened. It is plain that the weaker the acid is in the first place, the greater the relative diminution of strength. No perceptible change takes place with the strong acids unless the salt is added in excessive quantities. This principle may fre-

quently be applied in the case of weak acids, when it is desired to lessen their solvent action in quantitative precipitations, as that of zinc sulphide from acetic acid solutions.

Following the same reasoning, it is evident that the addition of a strong acid to the solution of a weak one lessens the ionization of the latter. This is of importance in a study of precipitations by sulphuretted hydrogen, which itself is a weak acid. An interesting example is that of the precipitation of zinc from its salts. If sulphuretted hydrogen is passed into a solution of zinc chloride a portion of the zinc is thrown down as sulphide, but the action soon ceases. This may be accounted for by the following considerations: 1. Zinc sulphide can only separate where the product of the concentration of the Zn and S ions in solution exceeds its solubility-product. 2. Sulphuretted hydrogen is but very slightly ionized. 3. As the zinc sulphide separates, hydrochloric acid is formed and is nearly completely ionized. 4. The presence of this strong acid (by increasing the concentration of the H ions) gradually lessens the ionization of the weak acid, sulphuretted hydrogen, just as sodium acetate lessens that of acetic acid, until the concentration of the S ions becomes so small that its product with the concentration of the Zn ions fails to equal or exceed the solubility-product of zinc sulphide, and precipitation must cease. But if zinc acetate is the salt used, the whole of the zinc is thrown down by sulphuretted hydrogen, because the acetic acid liberated is not a sufficiently strong acid to so far increase the concentration of the hydrogen ions, as to cause a diminution of the ionization of the sulphuretted hydrogen sufficient to cause the solubility-product of the zinc sulphide to fall below the critical value.

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The application of the law of mass action to the re-solution of precipitates may, after what has been stated, be well shown by an example; for instance, the solution of ferric hydroxide in hydrochloric acid. As no body is wholly

insoluble in water, a minute quantity of the hydroxide will first pass into solution *in water*, and in such a solution this substance will be ionized (slightly, as it is a weak base). The saturated solution will assume, for the moment, a condition of equilibrium parallel to that of barium sulphate, as stated on page 120, the ions being Fe and 3 (OH). But the latter will at once unite with the H ions of the hydrochloric acid to form water (undissociated), and in order to maintain the concentration of the OH ions more of the hydroxide must pass into solution. This process repeats itself with great rapidity until the hydroxide is all dissolved, or the acid saturated. Similarly, hydrochloric acid will dissolve calcium oxalate, because, by the union of the 2 H and C_2O_4 ions, some undissociated oxalic acid is formed, and more oxalate must pass into solution to replace the C_2O_4 ions so removed, and thus to restore the equilibrium. It must be noted here that saturation of hydrochloric acid with respect to the oxalate will occur much more quickly than with respect to the hydroxide, because the oxalic acid is relatively largely dissociated in comparison with water, and the solution after a time becomes saturated with Ca and C_2O_4 ions.

Again, acetic acid dissolves calcium phosphate because the phosphoric acid is less dissociated than acetic acid ; while calcium oxalate is not dissolved because the reverse is true. The slightly increased solubility of barium sulphate precipitates in the presence of hydrochloric acid is probably due, in the same way, to the lesser degree of dissociation of the sulphuric than the hydrochloric acid.

The re-solution of a precipitate is often occasioned by the formation of some complex ion in place of the simple ions formerly existing. Thus copper salts are dissolved by solutions containing ammonia with the formation of complex ions, silver salts in potassium cyanide, and so on. This must be taken into account in seeking for the explanation of the solubility of precipitates in special cases. Magnesium forms complex ions with ammonium compounds, which prevents the precipitation of its hydroxide by ammonia, a fact which is taken advantage of in qualitative and quantitative analysis.

It has already been stated that the water in aqueous solutions is but very slightly ionized. While this is true, it is also a fact that the H and OH ions of the dissociated water exert a distinct influence upon certain classes of salts — namely, those in which one or more of the ions is that of a very weak base or acid. For example, a solution of a neutral salt, as zinc sulphate, shows an acid reaction, because the ions of the salt, Zn and SO_4, together with the minute quantity of H and OH ions from the dissociated water, tend to form $Zn(OH)_2$ and H_2SO_4. The former is a very weak base, and accordingly is but little dissociated, and does not exhibit an alkaline reaction; while the sulphuric acid is, on the contrary, largely dissociated, and the concentration of the H ions in solution is sufficient to cause an acid reaction. The reverse process goes on with a salt of the character of potassium cyanide, from which KOH and HCN are formed. The latter is so weak an acid as to be but very slightly ionized; while the potassium hydroxide yields OH ions, which cause an alkaline reaction. This process, whereby the ions of the water enter into play with the ions of the substances in solution, is called *hydrolysis*.

The precipitation of a basic carbonate of zinc, mentioned on page 55, is the result of hydrolytic action of the water upon the zinc carbonate first formed, by which a portion is changed to hydroxide, which at first is held in colloidal solution (see page 12), and is then precipitated with the zinc carbonate upon boiling.

It has already been pointed out that the action of an acid upon an hydroxide is, in effect, merely the union of H and OH ions to form water. Such a reaction remains incomplete to an extent corresponding to the degree of dissociation of the water; but it must be again emphasized that this is very small, and usually beyond the limits of measurement permitted by the indicators in use. It is a fact, however, that the use of certain indicators is disturbed by secondary hydrolytic reactions, as is shown on page 130.

The indicators used in acidimetry or alkalimetry are organic bodies either weakly basic or acid in their character. Those compounds have been selected as indicators which furnish a colored ion when dissociated, or afford a colored solution when in the un-ionized state, whereby the change from the one to the other condition is made evident. For example, methyl orange is a compound belonging to a class of organic bodies known as sulphonic acids. In the free state the acid is but very little ionized, and the undissociated acid yields a pink solution. The moment that the acid is neutralized by alkali, a salt of the sulphonic acid is formed, which, in common with all salts, is at once dissociated, and the anion yields a yellow solution. The addition of even a drop of free mineral acid in excess, at once causes a combination of the H ions from this acid and the anions from the salt of the sulphonic acid, to form the non-dissociated sulphonic acid, with the return of the pink. This is the point chosen as the end-point.

Phenolphthalëin is another weak acid. It, however, presents a reverse behavior. The undissociated acid is colorless in solution, while the anion of the salt is pink. In the case of litmus the undissociated acid is red, the dissociated ion blue.

It is stated on page 72 that methyl orange may be used in cold solutions in the presence of carbonic acid and sulphuretted hydrogen, and will still indicate the point at which all the mineral acid present is neutralized. The other indicators require the previous expulsion of the carbon dioxide or sulphuretted hydrogen, by boiling. The acid of methyl orange, while still a weak acid, is yet stronger — *i. e.*, more largely dissociated — than carbonic acid, or sulphuretted hydrogen. Accordingly the concentration of the H ions of these latter acids is less than that of the H ions from an equivalent quantity of the sulphonic acid, and the former do not enter into combination with the OH ions of the base until after those of the sulphonic acid of the indicator — *i. e.*, until after a salt of the sulphonic acid has formed and the end-point has been reached.

The acid contained in phenolphthalëin, litmus, and the like, are weaker — *i. e.*, less dissociated — than carbonic acid or sulphuretted hydrogen. The latter, therefore, first furnish H ions to unite with the OH ions of the hydroxide, and no salt of the indicator acid is formed until these acids have been neutralized. It is accordingly necessary to expel these volatile acids by boiling, in the presence of an excess of mineral acid, in order to discover exactly the point at which the mineral acid is neutralized. Methyl orange is to be preferred as an indicator in alkalimetry, because it forms salts most readily with bases, and phenolphthalëin in acid-imetry, because it responds most readily to the influence of acids. Methyl orange is too strong an acid to be successfully used with the organic acids in general.

On the other hand, phenolphthalëin does not give accurate results with ammonia, or in the presence of ammonium salts (page 73). Ammonia is a weak base, and the salt which should be formed with the indicator undergoes hydrolysis, whereby, instead of the colored ion, the weak, undissociated acid of the indicator and undissociated base (ammonia) are formed, and it is only when a relatively considerable excess of the ammonia exists in solution, that the concentration of the OH ions becomes sufficiently large to overcome the hydrolytic action.

The reaction between sodium carbonate and a mineral acid presents some interesting features. When sodium carbonate is placed in aqueous solution the carbonic acid, owing to its tendency to pass into a less ionized state, gives rise to the formation of an ion HCO_3 in solution; that is, the sodium carbonate yields first the ions 2 Na and CO_3, and the latter, acting upon water, yield a certain proportion of HCO_3 and OH ions, the latter occasioning the alkaline reaction. When H and Cl ions are added to such a solution, in the form of hydrochloric acid, the H and OH ions first unite to form water, and as the OH ions disappear, more HCO_3 ions are formed from the CO_3 ions. This continues until all the CO_3 ions are transformed into HCO_3 ions, when the latter begin to interact with the H ions of the mineral acid to form undissociated H_2CO_3.

It is stated on page 81 that phenolphthalëin may be used as an indicator to show when one half the carbonate in a solution of an alkaline carbonate has been neutralized, provided the volume of water is sufficient to retain all the liberated carbonic acid in solution. From the foregoing it appears that the indicator forms a salt with the alkali as long as hydroxyl ions remain in the solution, but as soon as these are withdrawn to form undissociated water, the hydrogen ion of the carbonic acid unites with the anion of the phenolphthalëin to form the free, undissociated acid. As the carbonic acid is unstable, the carbon dioxide tends to escape even in the cold, and is completely removed with the steam from boiling solutions.

Sodium bicarbonate yields as ions Na and HCO_3, and does not, therefore, give an alkaline reaction with phenolphthalëin.* Upon boiling its solutions the ion is decomposed as follows: $Na + HCO_3 = Na + OH + CO_2$. The carbon dioxide escapes, and the solution contains a quantity of OH ions equivalent to that formed from one molecule of normal sodium carbonate for each two molecules of the bicarbonate. This is the explanation of the return of the color on boiling carbonate solutions, when phenolphthalëin or litmus is used as an indicator, as described on page 73.

As the end-points are sharper, the greater the difference between the degree of ionization of the indicator and that of the acid or base used for titration, it is better, in general, to use concentrated rather than very dilute solutions.

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* It is probably true that by hydrolytic action the $NaHCO_3$ is slightly dissociated into Na, OH, and HCO_3 ions, and that a minute quantity of the sodium salt of the indicator acid is formed, but so little that the hydrolytic action dissociates it. On the other hand, the amount of OH ions is sufficient to form salts with other indicators (as litmus) having stronger acids, the salts being, therefore, less subject to hydrolysis.

PART V.

STOICHIOMETRY.

The stoichiometrical problems with which the analytical chemist has to deal are not, as a rule, difficult either to solve or to comprehend. The student will find that a moderate time devoted to the thoughtful study of these problems will do much to prevent embarrassment in later professional experience, where the ability to make the necessary calculations for the interpretation of analytical data is no less important than the manipulative skill by which the data are obtained.

Detailed solutions of a few typical problems are given below. The student should study these carefully, and assure himself that they are fully understood.

1. A "chemical factor" expresses the ratio between a specific quantity of a chemical compound and the *equivalent* quantity of some other body. For example, if it is wished to determine the weight of sulphur which corresponds to a specific weight of barium sulphate, the latter is multiplied by the factor, or ratio, represented by the fraction $\dfrac{S}{BaSO_4}$, or $\dfrac{32.07}{233.50} = 0.1373$. It may also be expressed by the proportion $\overset{233.5}{BaSO_4} : \overset{32.07}{S} = $ wt. $BaSO_4$: x, from which it is plain that $x = \dfrac{32.07}{233.50} \cdot$ wt. $BaSO_4$.

Again, if the weight of FeO in Fe_2O_3 is desired, the factor becomes $\dfrac{2\ FeO}{Fe_2O_3} = \dfrac{144.04}{160.04} = 0.9000$. Similarly, the factor for the conversion of KCl to K_2O is $\dfrac{K_2O}{2\ KCl} = \dfrac{94.22}{149.12} = 0.6320$. The logarithmic equivalents of these values are called log factors.

In the calculation of these factors, the atomic or molecular relations of the two substances must be kept clearly in mind; thus, it is plainly *incorrect* to express the ratio of ferrous to ferric oxide by the fraction $\dfrac{FeO}{Fe_2O_3}$, since each molecule of the higher oxide must correspond to two molecules of the lower. Carelessness in this respect is one of the most frequent sources of error.

2. To calculate the volume of a reagent required for a specific operation, it is necessary to know the exact reaction which is to be brought about, and, as with the calculation of factors, to keep in mind the molecular relations between the reagent and the substance reacted upon. For example, to estimate the weight of barium chloride necessary to precipitate the sulphur from 0.1 gram of pure pyrite (FeS_2), the proportion should stand $2 \overset{488.70}{BaCl_2 . 2 H_2O} :$ $\overset{120.16}{FeS_2} = x : 0.1$, where x represents the weight of the chloride required. Each of the two atoms of sulphur will form a molecule of sulphuric acid upon oxidation, which, in turn, will require a molecule of the barium chloride for precipitation. To determine the quantity of the barium chloride required, it is necessary to include in its molecular weight the water of crystallization, since this is inseparable from the chloride when it is weighed. This applies equally to other similar instances.

If the strength of an acid is expressed in percentage by weight, due regard must be paid to its specific gravity. For example, hydrochloric acid (sp. gr. 1.12) contains 23.8 per cent. HCl by weight; *i. e.*, 0.2666 gram.

3. No rules for universal application to "indirect gravimetric analyses" can be laid down. A single example will be explained.

Given a mixture of KCl + NaCl weighing 0.15 gram, which contains 53 per cent. chlorine, to calculate the weight of KCl and of NaCl in the mixture.

The weight of chlorine in the mixture is (0.15 × 0.53) or 0.0795 gram. Assuming that this chlorine was all in combination with potassium, the corresponding weight of KCl would be 0.1672 gram (Cl : KCl = 0.0795 : 0.1672). This is an excess of 0.0172 gram over the actual weight of the mixture, and it is plain that this difference is occasioned by the replacement of certain of the molecules of potassium chloride, weighing 74.56 units, by molecules of sodium chloride weighing 58.50 units. To express this, let it be supposed that the mixture is made up of n molecules KCl and n' molecules NaCl; then it may be said that $n \overset{74.56}{KCl} +$ $n' \overset{58.50}{NaCl} = 0.15$ gram, and $n \overset{74.56}{KCl} + n' \overset{74.56}{KCl} = 0.1672$ gram, then by subtracting the first equation from the second it is shown that $n' (\overset{74.56}{KCl} - \overset{58.50}{NaCl}) = 0.0172$ gram. That is, the difference in weight is equal to n' times the difference in the molecu-

lar weights of the two chlorides. The actual weight of NaCl present (x) is equal to $58.50n'$, or, since $n' = \dfrac{0.0172}{74.56 - 58.50}$, $x = 58.50\left(\dfrac{0.0172}{74.56 - 58.50}\right)$. This may be expressed in the form $(74.56 - 58.50) : 58.50 = 0.0172 : x$, from which $x = 0.0626$. The weight of NaCl subtracted from that of the mixture gives the weight of KCl.

The weights of the chlorides may also be calculated algebraically by solving the equations $x + y = 0.15$ and $\dfrac{35.45}{74.56}x + \dfrac{35.45}{58.50}y = 0.0795$, where x is the weight of KCl and y is the weight of NaCl in the mixture.

4 It is sometimes desirable to weigh out such a quantity of substance for analysis, that the number of cubic centimeters of standard solution entering into the reaction shall represent directly the percentage of the desired constituent. This may be readily done, by considering the relation of the solution to a normal solution and the atomic or molecular weight of the desired component. For example, suppose it is desired to calculate such a weight for K_2CO_3 in pearlash, when a half-normal acid solution is used. Since half-normal acid and alkali solutions are equivalent, and since, by definition, the half-normal K_2CO_3 solution contains 34.55 grams per liter, each cubic centimeter of the acid solution must be equivalent to 0.03455 gram K_2CO_3. Hence, 100 cc. would neutralize 3.455 grams pure K_2CO_3, and this becomes the desired weight of the pearlash. Similarly, the required weight of limonite, where the iron (Fe) is to be determined by means of a deci-normal $K_2Cr_2O_7$ solution, is 0.5602 gram.

5. One of the most frequently recurring cases in volumetric analysis is that in which it is wished to express the value of a specific solution in terms of some substance other than that against which it has been standardized; as, for instance, the value of a permanganate solution which has been standardized against oxalic acid, in terms of iron. Although such problems apparently vary widely, there are common principles which can be applied to them all. These are stated below, and the student should assure himself that they are fully understood.

Suppose, for example, it is desired to find the iron value (Fe) of a permanganate solution, of which 1 cc. is equivalent to 0.0063 gram $C_2H_2O_4 . 2 H_2O$.

From a comparison of the reactions on page 94, it is seen that 10 molecules of ferrous sulphate and 5 molecules of oxalic acid each react with the same amount (2 molecules) of the permanganate. These two quantities being, then, equivalent to the same third quantity, must be equivalent to each other ; in other words, 10 molecules of ferrous sulphate and 5 molecules of oxalic acid have the same reducing power. But, as stated above, the value is desired in terms of metallic iron (Fe), not $FeSO_4$, but as it is plain that 10 $FeSO_4$ are equivalent to 10 Fe, it is proper to make the proportion

$$\overset{560.2}{10\ Fe}\ :\ 5\ \overset{630.25}{C_2H_2O_4}.\ 2\ H_2O\ =\ x\ :\ .006302$$

in which $x = 0.005602$ gram. Here, again, as in example 2, it is necessary to include the water of crystallization in the molecular weight of the oxalic acid, as it is weighed with it.

The same conclusion is arrived at, if we consider the relation of the solution to the normal. As given, it is deci-normal and must, therefore, be equivalent to a deci-normal solution of iron. From the equations cited, it is seen that 10 $FeSO_4$ unite with 5 O, therefore each molecule is equivalent to 1 hydrogen atom in reducing power. The normal solution must, then, contain 1 gram-molecule of ferrous sulphate, or 56.02 grams Fe, and each cubic centimeter of the deci-normal solution would contain 0.005602 gram, the value obtained above.

Again, suppose the value of the same permanganate solution were desired in terms of molybdenum (Mo), the reactions with permanganate being

$$5\ Mo_{12}O_{19}\ +\ 17\ Mn_2O_7\ =\ 60\ MoO_3\ +\ 34\ MnO,\ and$$
$$5\ C_2H_2O_4.\ 2\ H_2O\ +\ Mn_2O_7\ =\ 2\ MnO\ +\ 10\ CO_2\ +\ 15\ H_2O.$$
$$(Mn_2O_7\ is\ the\ anhydride\ of\ HMnO_4.)$$
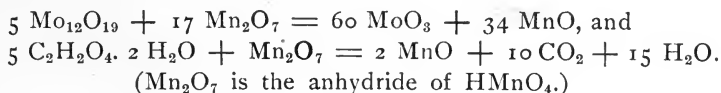
It is plain that in these equations as they stand, the molecular quantities of oxidizing agent are not equal. They can be made so by simply multiplying the second equation by 17, and they then become,

$$5\ Mo_{12}O_{19}\ +\ 17\ Mn_2O_7\ =\ 34\ MnO\ +\ 60\ MoO_3,\ and$$
$$85\ C_2H_2O_4.\ 2\ H_2O\ +\ 17\ Mn_2O_7\ =\ 34\ MnO\ +\ 170\ CO_2\ +$$
$$255\ H_2O.$$
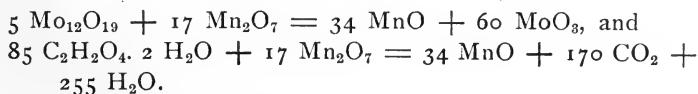
It is now possible to reason in the same way as before, and to conclude that 85 molecules of the oxalic acid have the same reduc-

ing power as 5 molecules of the oxide $Mo_{12}O_{19}$, or 60 atoms of molybdenum. Accordingly,

$$60 \overset{575.88}{Mo} : 85\ C_2H_2O_4. \overset{1071.25}{2}\ H_2O = x : 0.006302$$

in which $x = 0.0003387$ gram.

Since 5 $Mo_{12}O_{19}$ unite with 85 O, a normal solution of the former as a reducing agent, would contain $\frac{1}{10}$ of the 5 gram-molecules or 3.387 grams Mo, and the deci-normal solution 0.3387 grams per liter. This agrees with the values already obtained.

6. It is sometimes necessary to calculate the value of solutions according to the principles just explained, when several successive reactions are involved. Such problems may be solved by a series of proportions, but it is usually possible, after stating these, to eliminate the common factors and solve but a single one.

For example, suppose it is desired to express the value of a permanganate solution, of which 1 cc. = 0.008 gram iron (Fe), in terms of calcium oxide (CaO). The reactions involved in the volumetric determination of calcium are the following : $CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2\ NH_4Cl$; $CaC_2O_4 + H_2SO_4 + 2\ H_2O = CaSO_4 + C_2H_2O_4. 2\ H_2O$; $5\ C_2H_2O_4. 2\ H_2O + 2\ KMnO_4 + 3\ H_2SO_4 = K_2SO_4 + MnSO_4 + 10\ CO_2 + 18\ H_2O$.

From the considerations stated under 5, the following proportions may be made :

$$10\ Fe : 5\ C_2H_2O_4. 2\ H_2O = .008 : x$$
$$5\ C_2H_2O_4. 2\ H_2O : 5\ CaC_2O_4 = x : y$$
$$5\ CaC_2O_4 : 5\ CaO = y : z$$

Canceling the common factors, there remains simply

$$10 \overset{560.2}{Fe} : 5 \overset{280.4}{CaO} = .008 : z$$

Similarly, from the reactions given in note 6, page 103, the equivalent of the iodine liberated may be calculated in terms of MnO_2 as follows : Supposing the weight of iodine to be 0.5 gram, then

$$2\ I : 2\ KI = 0.5 : x$$
$$2\ KI : 2\ Cl = x : y$$
$$2\ Cl : 2\ HCl = y : z$$
$$2\ HCl : MnO_2 = z : w$$

Canceling the common factors, there remains

$$2\ I : MnO_2 = 0.5 : w$$

To solve such problems as 5 and 6, it is necessary to know the reactions involved, and the way in which the various components break up; then to compare the reactions and to search for those molecular quantities of the compounds in question, which are *equivalent* in their action upon a common agent. Having found these, as shown above, express the molecular ratio between them in the form of a proportion; as, for example, $2 \overset{253.7}{\text{I}} : \overset{86.99}{\text{MnO}} = 0.5 : w$. Expressed in the form $w = \dfrac{86.99}{253.7} \, 0.5$, it is plain that this ratio is in no way different in principle from the chemical factor mentioned in paragraph 1; indeed, it is the factor for the conversion of iodine to manganese dioxide.

PROBLEMS.

(The reactions necessary for the solution of these problems are either stated with the problem, or may be found in the earlier text. The atomic weights used are those given in the table on page 145.)

GRAVIMETRIC ANALYSIS.

1. Calculate the chemical factors for (*a*) $(NH_4)_2O$ from $2 (NH_4)Cl. PtCl_4$; (*b*) for K in $2 KCl. PtCl_4$; (*c*) for P in $Mg_2P_2O_7$; (*d*) for Fe_2O_3 from Fe_3O_4.
        Answers: (*a*) 0.1175, (*b*) 0.1611, (*c*) 0.2787, (*d*) 1.034.

2. If 0.5 gram of platinum remains after the ignition of the precipitate of the double salt, $2 NH_4Cl. PtCl_4$, derived from 1 gram of an ammonium compound, calculate the percentage of NH_3 in the latter. $2 NH_4Cl. PtCl_4 = 2 NH_3 + 2 HCl + 2 Cl_2 + Pt$.   *Answer:* 8.76 %.

3. What weight of Mn_3O_4 corresponds to 1 gram of $Mn_2P_2O_7$?
                Answer: 0.5375 gram.

4. How many cubic centimeters of aqueous ammonia (sp. gr. 0.96) containing 9.90 per cent. NH_3 by weight, will be required to precipitate the iron as $Fe(OH)_3$ from 1 gram of $(NH_4)_2SO_4$. $FeSO_4. 6 H_2O$?   *Answer:* 1.37 cc.

5. How many cubic centimeters of HNO_3 (sp. gr. 1.135) containing 20 per cent. HNO_3 by weight, are required to oxidize the iron in 1 gram of $FeSO_4. (NH_4)_2SO_4. 6 H_2O$, in the presence of sulphuric acid? $6 FeSO_4 + 2 HNO_3 + 3 H_2SO_4 = 3 Fe_2 (SO_4)_3 + 2 NO + 4 H_2O$.   *Answer:* 0.24 cc.

6. The ignited precipitate of $Fe_2O_3 + Al_2O_3$ from 1.5 grams of a silicate weighs 0.4069 gram; this mixture loses 0.0200 gram when ignited in hydrogen. What is the percentage of Fe_2O_3 and Al_2O_3 in the sample? $Fe_2O_3 + 3 H_2 = 2 Fe + 3 H_2O$.

Answer: 22.68 % Al_2O_3; 4.44 % Fe_2O_3.

7. How many cubic centimeters of "magnesia mixture" (64 grams $MgCl_2$ per liter) will be required to precipitate the arsenic from 0.2 gram As_2S_3, after oxidation to arsenic acid? $H_3AsO_4 + MgCl_2 + 3 NH_4OH = MgNH_4AsO_4 + 2 NH_4Cl + 3 H_2O$.

Answer: 2.42 cc.

8. How many cubic centimeters of an ammonium oxalate solution $[(NH_4)_2C_2O_4. H_2O]$ (40 grams per liter), are required to precipitate the calcium as oxalate from 1 gram of apatite $(Ca_3(PO_4)_2. CaCl_2)$? How many cubic centimeters of "magnesia mixture" (containing 64 grams $MgCl_2$ per liter) are necessary to combine with the phosphoric acid in the same weight of apatite? *Answer:* 33.73 cc. and 7.06 cc.

9. If a calcium oxalate precipitate (which is contaminated by silica) from 0.83 gram of dolomite be ignited under such conditions that the decomposition products may be passed through $Ba(OH)_2$ solution, and the resulting precipitate of barium carbonate be found, on drying, to weigh 0.9500 gram, what is the percentage of CaO in the sample? *Answer:* 32.51 %.

10. How many cubic centimeters of a potassium tetroxalate solution $(KHC_2O_4. C_2H_2O_4. 2 H_2O)$, containing 50 grams per liter, would be required to precipitate the calcium from 1 gram of a sample of dolomite yielding 2 % Fe_2O_3, 10 % MgO, and 45 % CO_2, assuming the iron, magnesium, and calcium to be present wholly as carbonates, the iron as ferrous carbonate?

Answer: 19.05 cc.

11. How many cubic centimeters of sulphuric acid (sp. gr. 1.75), containing 81 per cent. H_2SO_4 by weight, are necessary to replace the nitric acid in the nitrates formed from 5 grams of a brass containing 65 % Cu, 34.5 % Zn and 0.5 % Pb?

Answer: 5.37 cc.

12. If 5.23 grams of brass yield 0.0345 gram $PbSO_4$, and subsequently 0.0031 gram PbO_2 on electrolysis of the filtrate, what is the percentage of Pb in the brass? *Answer:* 0.5 %.

13. If in the analysis of a brass containing 65 % copper, an error is made in weighing a 5-gram portion, by which 0.001 gram

too much is weighed out, what would be the percentage of copper, as determined? If the same error is made in weighing 0.2 gram of apatite containing 40 % P_2O_5, what will be the apparent percentage? What will be the percentage error in each case?

Answers: 65.01 % Cu; 40.2 % P_2O_5; 0.02 % and 0.5 %.

14. If the dry cupric sulphide from 0.82 gram of brass loses 0.1345 gram on ignition in hydrogen, what is the percentage of copper in the brass? $2 CuS = Cu_2S + S.$ *Answer:* 65.05 %.

15. If 1.5 grams of glass yield 0.38 gram KCl + NaCl, from which 0.646 gram $2 KCl. PtCl_4$ is obtained, what is the percentage of Na_2O in the glass? *Answer:* 6.43 %.

16. A mixture of BaO and CaO weighing 0.2438 gram yields 0.4876 grams of mixed sulphates. What is the weight of each oxide in the original mixture?

Answer: 0.1288 gram CaO; 0.1150 gram BaO.

17. Calculate the percentage of pure Na_2CO_3 in an impure sample, from the following data: Crucible + SiO_2 = 20.0697 grams; crucible + SiO_2 + Na_2CO_3 (impure) = 20.3264 grams; crucible + SiO_2 (excess) + Na_2SiO_3 (after fusion) = 20.2239 grams. Assume the reaction to be $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$ *Answer:* 96.25 %.

18. A sample of pyrite weighing 0.5 gram yields 1.6 grams $BaSO_4$. Calculate the percentage FeS_2 in the sample.

Answer: 82.35 %.

VOLUMETRIC ANALYSIS.

1. How much crude cream of tartar should be taken for an analysis in order that the number of cubic centimeters of $\frac{N}{2}$ NaOH solution required to react with it, shall represent directly the percentage of $KHC_4H_4O_6$? How much oxalic acid in order that each cubic centimeter of $\frac{N}{10}$ $KMnO_4$ may represent 1 % $C_2H_2O_4$. $2 H_2O$? $KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O.$

Answer: 9.409 gram $KHC_4H_4O_6$; 0.6302 gram $C_2H_2O_4$. $2 H_2O$.

2. What weight of potassium ferrocyanide, $K_4Fe(CN)_6$. $3 H_2O$, should a normal solution contain, for use as a reducing agent? $10 K_4Fe(CN)_6. (3 H_2O) + 2 KMnO_4 + 8 H_2SO_4 = 10 K_3Fe(CN)_6 + 6 K_2SO_4 + 2 MnSO_4 + 8 H_2O + (30 H_2O).$

3. Calculate the percentage of carbon dioxide (CO_2) in a sample of calcium carbonate from the following data :

Total volume $\frac{N}{2}$ HCl $= 35$ cc.; total volume $\frac{N}{10}$ NaOH $= 15$ cc.; weight carbonate $= 1.00$ gram. *Answer :* 35.20%.

4. Calculate the weight of $KHC_2O_4. C_2H_2O_4. (2 H_2O)$ necessary for a liter of normal solution, (*a*) as a standard acid solution (compare note 7, on page 79), (*b*) as a reducing agent. $KHC_2O_4. C_2H_2O_4. (2 H_2O) + 2 MnO_2 + 3 H_2SO_4 = 2 MnSO_4 + KHSO_4 + 4 CO_2 + 4 H_2O + (2 H_2O)$.

Answer : (*a*) 84.72 ; (*b*) 63.54 grams.

5. Given the following data, calculate the percentage purity of the oxalic acid :

Standardization : Weight $CaCO_3 = 1.050$ gram ; HCl solution used $= 45$ cc. ; NaOH solution used $= 4.8$ cc. ; 1 cc. NaOH solution $= 1.042$ cc. HCl solution.

Analysis : Weight oxalic acid $= 1.500$ gram ; NaOH solution used $= 42.5$ cc. ; HCl solution used $= 0.5$ cc.

Answer : 96.52 $\%$.

6. Given the following data, calculate the percentage purity of the cream of tartar ($KHC_4H_4O_6$) :

Weight of substance $= 2.500$ grams ; NaOH solution used $= 25.51$ cc. ; H_2SO_4 solution used $= 0.5$ cc. ; 1 cc. H_2SO_4 solution $= 1.02$ cc. NaOH solution ; 1 cc. NaOH solution $= 0.0255$ gram $CaCO_3$. *Answer :* 95.90 $\%$.

7. Solutions of alkali carbonates with phenolphthalëin become colorless as soon as the carbonate has changed to bicarbonate. Calculate the percentage NaOH in a sample of soda ash from the following data, assuming the hydrate to be neutralized before the carbonate is attacked : Weight of soda ash $= 1$ gram ; HCl solution is $\frac{N}{2}$. The solution becomes colorless when 25 cc. HCl have been added, but requires 40 cc. for complete neutralization, after boiling out the carbon dioxide. $Na_2CO_3 + HCl = HNaCO_3 + NaCl$; $NaHCO_3 + HCl = NaCl + CO_2 + H_2O$.

Answer : 20.02 $\%$.

8. If 10 cc. of a sulphuric acid solution yield 0.1220 gram $BaSO_4$, how much must the solution be diluted for an exactly $\frac{N}{10}$ solution ? *Answer :* 1000 cc. to 1044 cc.

9. If 1 cc. of a potassium bichromate solution will oxidize 0.0066 gram iron, to what volume must 100 cc. of the solution be diluted to make a $\frac{N}{100}$ solution ? *Answer :* 100 cc. to 1178 cc.

10. Calculate the percentage of iron (Fe) in a sample of limonite from the following data:

Weight of limonite = 0.55 gram; $K_2Cr_2O_7$ solution used = 51.1 cc.; 1 cc. $K_2Cr_2O_7$ solution = .0058 gram Fe; $FeSO_4$ solution used = 5 cc.; 5 cc. of $FeSO_4$ solution contains 0.008 gram FeO. *Answer:* 52.74 %.

11. A sample of iron wire is dissolved, out of contact with air, in 30 cc. HCl, of which 1 cc. = 0.95 cc. $\frac{N}{2}$ HCl. The iron requires 40 cc. $\frac{N}{10}$ $K_2Cr_2O_7$ for oxidation. What excess of HCl was used over that required for solution? *Answer:* 13.16 cc.

12. How much stannous chloride ($SnCl_2$) by weight will it require to reduce the iron from 0.5 gram magnetite ($FeO. Fe_2O_3$), dissolved out of contact with air? *Answer:* 0.4093 gram.

13. How many cubic centimeters of HCl (sp. gr. 1.12) are required to dissolve 0.55 gram limonite ($2 Fe_2O_3. 3 H_2O$), assuming the only impurity to be 1.5 per cent. quartz?

Answer: 2.37 cc.

14. If 0.75 gram of a silicate yields 0.4 gram $Fe_2O_3 + Al_2O_3$, and the iron present requires 20 cc. $K_2Cr_2O_7$ solution (1 cc. = 0.0784 gram $FeSO_4(NH_4)_2SO_4. 6 H_2O$), calculate the percentage FeO and Al_2O_3 in the sample.

Answer: 38.37 % FeO; 10.72 % Al_2O_3.

15. What weight of iron wire containing 99.85 % Fe will react with the chromium from 0.5 gram chromite ($FeO. Cr_2O_3$)?

Answer: 0 7504 gram.

16. If 1 cc. of a potassium permanganate solution will oxidize 0.0085 gram Fe, calculate the value of the same solution in terms of (*a*) $KHC_2O_4.C_2H_2O_4. 2 H_2O$; (*b*) KNO_2; (*c*) Mn; (*d*) $K_4Fe(CN)_6. 3 H_2O$.

$10 KHC_2O_4. C_2H_2O_4. (2 H_2O) + 8 KMnO_4 + 17 H_2SO_4 = 9 K_2SO_4 + 8 MnSO_4 + 40 CO_2 + 32 H_2O + (20 H_2O)$; $10 KNO_2 + 4 KMnO_4 + 11 H_2SO_4 = 7 K_2SO_4 + 4 MnSO_4 + 10 HNO_3 + 6 H_2O$; $3 MnO + Mn_2O_7 = 5 MnO_2$, and $2 KMnO_4 = K_2O. Mn_2O_7$; compare also problem 2.

Answer: (*a*) 0.009640 gram; (*b*) 0.006463 gram; (*c*) 0.002502 gram; (*d*) 0.06414 gram.

17. Calculate the value of a permanganate solution, of which 1 cc. = 0.008 gram Fe, in terms of MoO_3. $Mn_2O_7 + 10 FeO = 5 Fe_2O_3 + 2 MnO$; $7 Mn_2O_7 + Mo_{24}O_{37} = 24 MoO_3 + 14 MnO$. *Answer:* 0.007051 gram.

18. Given the following data, calculate the percentage of iron in the limonite :

Weight of limonite $= 0.55$ gram; $KMnO_4$ solution used $= 30$ cc.; 1 cc. $KMnO_4$ solution $= 0.0084$ gram $C_2H_2O_4 . 2 H_2O$.

Answer: 40.74 %.

19. The calcium oxalate precipitate from 0.5 gram marble, when treated with sulphuric acid, liberates sufficient oxalic acid to reduce 43 cc. of permanganate solution (1 cc. $= 0.01150$ gram Fe). Calculate the percentage of calcium (Ca) in the marble.

Answer: 35.38 %.

20. If 1 cc. $KMnO_4$ solution will oxidize 0.008 gram iron (Fe), calculate the equivalent of the same solution in terms of hydrogen peroxide (H_2O_2), and also the volume of oxygen which will be evolved by each cubic centimeter of the permanganate solution during the reaction, assuming that 1 cc. of oxygen weighs 0.00143 gram under the existing conditions. $5 H_2O_2 + 2 KMnO_4 + 3 H_2SO_4 = K_2SO_4 . + 2 MnSO_4 + 5 O_2 + 5 H_2O$.

Answer: 0.002431 gram; 1.6 cc.

21. Given the following data, calculate the percentage of MnO_2 in the pyrolusite :

Weight of pyrolusite $= 0.48$ gram ; weight $FeSO_4 . (NH_4)_2SO_4 . 6 H_2O = 4.3501$ grams; $K_2Cr_2O_7$ solution used $= 10$ cc.; 1 cc. $K_2Cr_2O_7$ solution $= 0.005$ gram Fe.

Answer: 92.45 %.

22. Given the following data, calculate the percentage of MnO_2 in the pyrolusite :

Weight pyrolusite $= 0.48$ gram; weight iodine liberated from $KI = 1.296$ grams.

For reactions, see note 6, page 103. *Answer:* 92.62 %.

23. If 1 cc. iodine solution is equivalent in oxidizing power to 0.00149 gram $KBrO_3$, to what volume must 100 cc. be diluted to make a $\frac{N}{20}$ solution ?

Answer: 107 cc.

24. Calculate the percentage purity of the sample of potassium bichromate from the following data :

Weight of sample $= 0.1237$ gram; $Na_2S_2O_3$ solution used $= 25$ cc.; 1 cc. $Na_2S_2O_3$ solution $= 1.004$ cc. iodine solution ; 1 cc. iodine solution $= 0.004975$ gram As_2O_3.

$K_2Cr_2O_7 + 6 KI + 7 H_2SO_4 = 4 K_2SO_4 + Cr_2(SO_4)_3 + 3 I_2 + 7 H_2O$.

Answer: 100 %.

25. Calculate the percentage purity of a sample of potassium iodate (KIO_3) from the following data:

Weight of sample $=$ 0.25 gram; $Na_2S_2O_3$ solution used $=$ 50 cc.; 1 cc. $Na_2S_2O_3$ solution $=$ 0.015 gram I. *Answer:* 84.34 %.

26. If 1 cc. of an iodine solution has the same oxidizing power as 0.0034 gram KIO_3, calculate its value in terms of antimony (Sb). *Answer:* 0.005742 gram.

27. What is the relation of each of the following solutions to a normal solution of the reagent?

$Na_2S_2O_3$. 5 H_2O : 1 cc. $=$ 0.001783 gram KIO_3.

$KMnO_4$ (acid solution): 1 cc. $=$ 0.006303 gram $C_2H_2O_4$. 2 H_2O.

As_2O_3 (as a reducing agent): 1 cc. $=$ 0.01772 gram Cl.

As_2O_3 (as an acid): 1 cc. $=$ 0.01061 gram Na_2CO_3.

NaOH : 1 cc. $=$ 0.1694 gram KHC_2O_4. $C_2H_2O_4$. 2 H_2O.

CAPACITY OF LIPPED BEAKERS

(REFERRED TO IN THE TEXT)

WHEN FILLED TO LOWER EDGE OF LIP.

No. 1 . . . . 120 CC.
No. 2 . . . . 210 CC.
No. 3 . . . . 310 CC.
No. 4 . . . . 540 CC.
No. 5 . . . . 700 CC.
No. 6 . . . . 930 CC.

TABLE OF ATOMIC WEIGHTS.*

$$O = 16.00.$$

Aluminum	. .	Al	27.11	Mercury . . .	Hg	200.0
Antimony	. .	Sb	120.43	Molybdenum .	Mo	95.98
Argon	A	?		Neodymium . .	Nd	140.5
Arsenic	. . .	As	75.09	Nickel	Ni	58.69
Barium	. . .	Ba	137.43	Nitrogen . . .	N	14.04
Bismuth	. . .	Bi	208.11	Osmium . . .	Os	190.99
Boron	B	10.95		Oxygen . . .	O	16.0
Bromine	. . .	Br	79.95	Palladium . .	Pd	106.36
Cadmium	. .	Cd	111.93	Phosphorus . .	P	31.02
Cæsium	. . .	Cs	132.89	Platinum . . .	Pt	194.89
Calcium	. . .	Ca	40.08	Potassium . .	K	39.11
Carbon	. . .	C	12.01	Praseodymium .	Pr	143.5
Cerium	. . .	Ce	140.2	Rhodium . . .	Rh	103.01
Chlorine . . .	Cl	35.45		Rubidium . .	Rb	85.43
Chromium	. .	Cr	52.14	Ruthenium . .	Ru	101.68
Cobalt	. . .	Co	58.93	Samarium . .	Sm	150.0
Columbium . .	Cb	94.0		Scandium . . .	Sc	44.0
Copper	. . .	Cu	63.60	Selenium . . .	Se	79.0
Erbium	. . .	Er	166.3	Silicon . . .	Si	28.40
Fluorine . . .	Fl	19.03		Silver	Ag	107.92
Gadolinium . .	Gd	156.1		Sodium . . .	Na	23.05
Gallium . . .	Ga	69.0		Strontium . .	Sr	87.61
Germanium . .	Ge	72.3		Sulphur . . .	S	32.07
Glucinum	. .	Gl	9.08	Tantalum . . .	Ta	182.6
Gold	Au	197.24		Tellurium . . .	Te	127.0
Helium . . .	He	?		Thallium . . .	Tl	204.15
Hydrogen	. .	H	1.0075	Thorium . . .	Th	232.63
Indium . . .	In	113.7		Tin	Sn	119.05
Iodine	I	126.85		Titanium . . .	Ti	48.15
Iridium . . .	Ir	193.12		Tungsten . . .	W	184.84
Iron	Fe	56.02		Uranium . . .	U	239.59
Lanthanum . .	La	138.6		Vanadium . .	V	51.38
Lead	Pb	206.92		Ytterbium . .	Yb	173.0
Lithium . . .	Li	7.03		Yttrium . . .	Y	88.95
Magnesium . .	Mg	24.29		Zinc	Zn	65.41
Manganese . .	Mn	54.99		Zirconium . .	Zr	90.6

* F. W. Clarke, *J. Am. Chem. Soc.*, **18**, 213.

STRENGTH OF REAGENTS.*

GRAMS PER LITER.

Ammonium Molybdate † (of MoO_3) . . . . . . 68 grams.
Ammonium Oxalate, $(NH_4)_2C_2O_4. H_2O$ . . . . 40 grams.
Barium Chloride, $BaCl_2$. 2 H_2O . . . . 20 grams.
Magnesium Ammonium Chloride (of $MgCl_2$) . . . 64 grams.
Mercuric Chloride, $HgCl_2$ . . . . 50 grams.
Potassium Hydroxide, KOH (sp. gr. 1.27) . . . . 480 grams.
Potassium Sulphocyanate, KSCN . . . . 5 grams.
Silver Nitrate, $AgNO_3$ . . . . 25 grams.
Sodium Hydroxide, NaOH . . . . 100 grams.
Sodium Carbonate, Na_2CO_3 . . . . 150 grams.
Sodium Phosphate, HNa_2PO_4. 12 H_2O . . . . . 100 grams.
Stannous chloride, $SnCl_2$, made by saturating hydrochloric acid
  with tin, diluting with an equal volume of water, and adding
  a slight excess of acid from time to time. A strip of metallic
  tin is kept in the bottle.

Aqueous ammonia, sp. gr. 0.96 contains 9.90% NH_3 by weight,
at 15° C.‡

Aqueous ammonia, sp. gr. 0.90 contains 28.30% NH_3 by weight,
at 15° C.‡

  Ammonia (0.96) may be prepared by diluting four volumes of ammonia
    (0.90) with seven volumes of water.

Hydrochloric acid, sp. gr. 1.12, contains 23.8% HCl by weight,
at 15° C.§

Hydrochloric acid, sp. gr. 1.20, contains 39.1% HCl by weight,
at 15° C.§

  Hydrochloric acid (1.12) may be prepared by diluting five volumes of
    hydrochloric acid (1.20) with four volumes of water.

Nitric acid, sp. gr. 1.20, contains 32.4% HNO_3 by weight, at
15° C.‖

Nitric acid, sp. gr. 1.42, contains 69.8% HNO_3 by weight, at
15° C.‖

  Nitric acid (1.20) may be prepared by diluting two volumes of nitric
    acid (1.42) with three volumes of water.

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* The concentrations given in this table are those upon which the proce-
dures in the foregoing pages are based. It is obvious, however, that an exact
adherence to these quantities is not essential.

† This solution is prepared according to the formula of Blair and Whitfield,
J. Am. Chem. Soc., **17**, 760.

‡ Lunge and Wiernik, *Ztschr. angew. Chem*, **1889**, 183.

§ Lunge and Marschlewski, *Ztschr. angew. Chem*, **1891**, 133.

‖ Kolb. *Dingl. pol. J.*, **182**, 233.

LOGARITHMS OF NUMBERS.

Natural numbers.	O	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
													Proportional Parts.						
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	103`	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS.

Loga-rithms	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											...								

Loga-rithms	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	3	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	3	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS.

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

INDEX.